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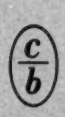

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PRECISION IN SPECTROPHOTOMETRY

COMMUNICATION 1. ERRORS IN SPECTROPHOTOMETRIC MEASUREMENTS

G. S. Tereshin

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Measurement of optical density, or, more accurately, determination of the spectrophotometer reading for the test solution, is the final operation in spectrophotometric analysis. In a number of cases, it is precisely this operation that limits the precision of an analysis. The problem we have set ourselves is to consider the sources of error in the measurements of the readings of a photoelectric spectrophotometer, and to show how this error depends on the reading itself.

A number of detailed articles [1-4] have been devoted to this problem. In our work we have not considered systematic errors determined by the non-proportionality of the electric current and the light energy, by the fact that the light is not sufficiently monochromatic, by incorrect calibration of the scale, by difference in absorption and by the length of the cuvette,etc., since these errors do not affect the precision of measurements of the spectrophotometer reading , but of the optical density. We are concerned not with errors in measuring the optical density (or transmittance) but the errors in reading the spectrophotometer, because an analysis is carried out on the basis of the spectrophotometer readings, which can differ considerably from the true values of the optical density as a result of systematic errors.

In the present article T and D designate, respectively, the readings of the transmittance scale and the optical density scale.

It has been repeatedly pointed out [5-8] that the errors in measuring the readings of the transmittance scale on spectrophotometers with electrical compensation do not depend on the readings of the scale T. It was precisely under this condition that the optimum readings of the spectrophotometer have been determined [5, 7]. Calculation of the errors during setting up of the transmittance scale on 0 and 100 gives only insignificant corrections [2, 9].

Sources of Errors During Measurement of Spectrophotometer Readings

It is necessary to distinguish two independent sources of error in the measurements:

1. The nonreproducibility of the spectrophotometer readings during photometric measurements of the same object (cuvette + solution) in the same position. In this case the error $\sigma_{T_{sp.}}$ (we shall call it the instrumental error) is determined by insufficient sensitivity of the spectrophotometer and the inability of the eye to establish absolutely accurately the position of the pointer on the scale.

2. The nonreproducibility of the cuvette during repeated filling with solution. This error $\sigma_{T_{gk}}$ (cuvette error) is determined by the impossibility of placing the cuvette in exactly the same place, and maintaining constant absorption (as a result of variations in the cleanliness of the cuvette and small corrosion of its surface).

The errors indicated are independent of each other. Accordingly, the dispersion of the total error of measurement is equal to the sum of the dispersion of its components:

$$\sigma_T^2 = \sigma_{T_{sp}}^2 + \sigma_{T_{gk}}^2; \quad (1)$$

the transmittance scale is expressed by the formula:

$$\sigma_1 = \sqrt{\sigma_{T_{sp}}^2 + \sigma_{T_{gk}}^2} \tag{2}$$

Let us consider the indicated components of the total error separately.

Spectrophotometer. All these discussions relate to a spectrophotometer with electrical compensation (SF-4 spectrophotometer, Beckman spectrophotometer, etc.). The error in the reading of the transmittance scale σ_T is considered for two reasons: 1) the transmittance scale is uniform; 2) the sensitivity of the spectrophotometer with respect to the transmittance scale is independent of T.

The sensitivity of a spectrophotometer s is equal to the ratio of the deflection of the milliammeter needle from an arbitrary zero (in milliammeter scale divisions) to the shift in the transmittance scale in divisions (1 division corresponds to 1 absolute percent transmittance) causing this deflection ([10], p. 68). For a constant position of the potentiometer, the sensitivity s does not depend on the readings of the transmittance scale; we confirmed this experimentally. Normally, a fairly high sensitivity (greater than 2) is used during measurements. Measurement of the transmittance consists of three independent stages, each of which gives a corresponding error.

A. Setting the Transmittance Scale on Zero (compensation of the dark current). In this case the error is determined by inaccuracy in setting the milliammeter needle on zero because of apparatus instability $\sigma_{(ma)instab.}$ and by inaccuracy in visually determining the position of the milliammeter needle at zero $\sigma_{(ma)vis.}$

The total error (in milliammeter divisions)

$$\sigma_{(ma)} = \sqrt{\sigma_{(ma)instab}^2 + \sigma_{(ma)vis}^2} \tag{3}$$

does not depend on T.

The error determined by inaccurate setting of the milliammeter needle on the zero, in transmittance scale divisions, is expressed by the formula:

$$\sigma_{T\,sens} = \frac{1}{s}\sigma_{(mA)} \tag{4}$$

$\sigma_{T_{sens.}}$ only depends on the sensitivity of the spectrophotometer. During measurement of the transmittance T, the error arising from inaccurate setting of the transmittance scale on zero is given by

$$\sigma_{T_0} = (1 - T)\,\sigma_{T\,sens} \tag{5}$$

since scale T is uniform, while at the point T = 1, the error $\sigma_{T_0} = 0$ (this point is established independently).

B. Setting the Transmittance Scale at 1.0 (with the switch "on"). In this case the error is again only determined by $\sigma_{T_{sens.}}$. The error in measuring the transmittance because of inaccurate setting on 1.0 is given by

$$\sigma_{T_1} = T\sigma_{T\,sens} \tag{6}$$

(at the point T =), the error $\sigma_{T_1} = 0$).

C. Reading the Transmittance T. During reading of T the error not only depends on the inaccuracy of the setting of the milliammeter needle on zero, but also on the error $\sigma_{T_{vis.}}$ of the visual reading of the transmittance scale:

$$\sigma_{T_{read}} = \sqrt{\sigma_{T_{sens}}^2 + \sigma_{T_{vis}}^2}. \tag{7}$$

The total instrumental error during a single measurement of the transmittance of the same photometrically measured object is expressed by the formula:

$$\sigma_{T_{sp}} = \sqrt{\sigma_{T_0}^2 + \sigma_{T_1}^2 + \sigma_{T_{read}}^2}. \quad (8)$$

Substituting equations (5), (6), and (7), and transforming, we get

$$\sigma_{T_{sp}} = \sqrt{\sigma_{T_{vis}}^2 + 2(T^2 - T + 1)\sigma_{T_{sens}}^2}. \quad (9)$$

This formula differs from the equation derived by Gridgeman [2],

$$\sigma_T = \sigma_{T_{read}} \sqrt{2(T^2 - T + 1)}, \quad (10)$$

since Gridgeman expressed the error arising from inaccurate setting at 0 and 1 by the error in reading $\sigma_{T_{read}}$. This, obviously, is not correct, since it is not taken into account that the error of the visual reading $\sigma_{T_{vis}}$, which affects the accuracy of taking the readings, does not affect σ_{T_0} and σ_{T_1}, while the error $\sigma_{T_{vis}}$ is fairly high in comparison with $\sigma_{T_{sens}}$ when the sensitivity of the apparatus is high. It should be pointed out that Gridgeman, in general, did not analyze the error in taking the reading, which he considered to be independent of T.

Formula (9) shows that $\sigma_{T_{sp}}$ depends on T to a lesser extent than Gridgeman indicated. It can be shown that at a high sensitivity s (about 2 and higher), when

$$\sigma_{T_{sens}} < \sigma_{T_{vis}}, \quad (11)$$

the instrumental error throughout the whole range of T does not change by more than 8%, i.e., to a certain approximation it can be considered that $\sigma_{T_{sp}}$ is independent of T. But, even at low sensitivity, (greater than $\sigma_{T_{sens}}$), the instrumental error only changes by 13%. Accordingly, henceforth we shall consider

$$\sigma_{T_{sp}} = \text{const} \quad (12)$$

(for a constant sensitivity of the apparatus).

The rules governing the choice of spectrophotometer sensitivity will be considered in a separate article.

The error in measuring the readings of the optical density scale is determined by the well known equation

$$\sigma_D = \frac{0{,}43\sigma_T}{T}. \quad (13)$$

This means that

$$\sigma_{D_{sp}} = \frac{0{,}43\sigma_{T_{sp}}}{T}. \quad (14)$$

$\sigma_{D_{sp}}$ rapidly increases with increasing D (Fig. 1, Curve 1).

Cuvettes. The second source of random errors in measuring the transmittance is the nonreproducibility of the state of the cuvette. Hitherto, the effect of this source of error on the precision of a measurement has not been expressed mathematically.

The transmittance measured is the product of the transmittance of the solution T_{soln} (with respect to a standard solution) and the transmittances of the cuvette with respect to each other T_{cuv}:

$$T = T_{soln} \cdot T_{cuv} \quad (15)$$

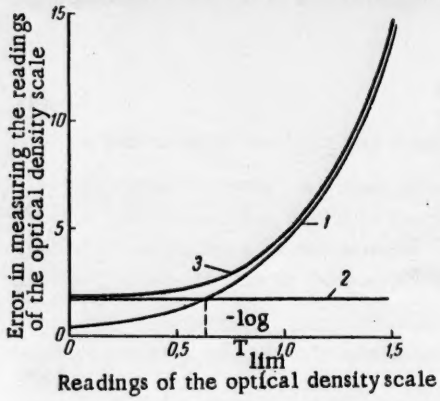

Fig. 1. The error in measuring the readings of the optical density scale: $\sigma_{T_{sp.}}$ = 1 (arbitrary), $T_{limit.} = 1/4$ 1) $\sigma_{D_{sp.}}$; 2) $\sigma_{D_{cuv.}}$; 3) σ_D.

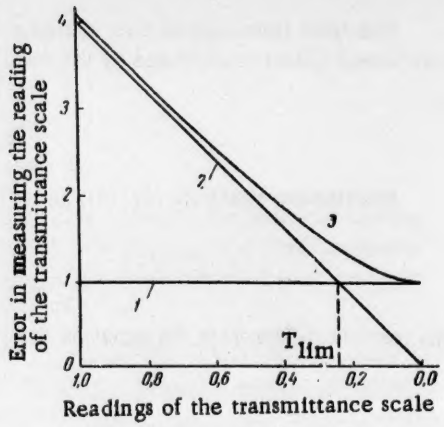

Fig. 2. The error in measuring the readings of the transmittance scale: $\sigma_{T_{sp.}}$ = 1 (arbitrary); $T_{limit} = 1/4$; 1) $\sigma_{T_{sp.}}$; 2) $\sigma_{T_{gk}}$; 3) σ_T.

The transmittance of the solution is constant.

The error in the reading of the transmittance scale caused by the nonreproducibility in the state of the cuvette ([11] p. 93) (the index g shows that this is an error in the scale reading, and not an error in measuring the transmittance of the cuvette):

$$\sigma_{T_{gk}} = T_{soln} \cdot \sigma_{T_{cuv}} \tag{16}$$

where $\sigma_{T_{cuv.}}$ is the mean square deviation of the transmittances of the cuvette relative to one another on changing the solution, and is independent of the transmittance of the solution. $T_{cuv.} \approx 1$, and, consequently, [from Formula (15)] $T_{soln.} = T$. Accordingly,

$$\sigma_{T_{gk}} = T \cdot \sigma_{T_{cuv}} \tag{17}$$

Thus, the error in the reading of the transmittance scale caused by the nonreproducibility of the state of the cuvette is strongly dependent on T: it decreases with decreasing T (Fig. 2, Curve 2). At the same time, the corresponding error in the readings of the optical density scale [from Formulas (13) and (17)].

$$\sigma_{D_{gk}} = 0{,}43\,\sigma_{T_{cuv}} = \sigma_{D_{cuv}} \tag{18}$$

does not depend on the readings of the spectrophotometer, and is equal to the mean square deviation of the optical densities of the cuvette relative to each other on changing the solutions.

The Total Error in Measuring the Spectrophotometer Readings

We shall find the total error in measuring the readings on the transmittance scale by substituting equation (17) in Formula (2)

$$\sigma_T = \sqrt{\sigma^2_{T_{sp}} + T^2\sigma^2_{T_{cuv}}} \tag{19}$$

In a similar way, it is possible to find the total error of measuring the reading of the optical density scale (from (13) and (19));

$$\sigma_D = 0{,}43\sqrt{\frac{\sigma^2_{T_{sp}}}{T^2} + \sigma^2_{T_{cuv}}} \tag{20}$$

From equations (19) and (20) it follows that the error in measuring the reading of the spectrophotometer depends on the reading itself (Fig. 1 and 2, Curve 3).

Experimental Verification of the Equation for the Measurement Error on the Spectrophotometer

Special measurements were made on a SF-4 spectrophotometer with the aim of a) demonstrating the reality of the existence of the cuvette error in measurement, b) confirming the theoretical equation derived for the total error of measurement, and c) finding and comparing $\sigma_{T_{sp.}}$ and $\sigma_{T_{cuv.}}$.

Six solutions of titanium sulfate with the following concentrations were prepared: 1)12.0; 2) 13.0; 3) 14.2; 4) 15.9; 5) 19.8, and 6) 31.5 mg of titanium in 100 ml of solution. Each 100 ml of solution also contained 5 ml of 20% hydrogen peroxide, 20 g H_2SO_4, and 0.5-1.0 g of $(NH_4)_2SO_4$. These solutions were photometrically measured with respect to a similar solution of the peroxide complex of titanium with a concentration of 12.0 mg of Ti in 100 ml. The same pair of rectangular cuvettes with a thickness of $l = 1.003$ cm for the absorbing layer was used. The external optical surfaces of the cuvettes were washed with distilled water and alcohol and then wiped with cambric. When the solutions were changed around the standard solution was changed first. The wavelength of 408 mμ corresponded to the maximum on the absorption curve for the peroxide complex of titanium. The slit width of the monochromator was 0.22 mm (this corresponded to a width of the spectral interval of 2.2 μ). The sensitivity of the apparatus was $s = 2.5$.

In order to exclude the effect of possible changes in the operating conditions of the apparatus with time, the solutions were photometrically measured in a definite sequence (the method of symmetrical observations [10]): solution 1, 2, 3, 4, 5, 6 (first filling of the cuvette); 6, 5, 4, 3, 2, 1 (second filling of the cuvette; 1 . . . 6 (third filling of the cuvette); 6, . . . 1 (fourth filling of the cuvette). In all, each solution was changedfour times, $m = 4$.

The results obtained were subjected to analysis of variance according to the following scheme.

During photometric measurement (as is usually done in practice) $n = 3$ single readings of T_i were made, and the mean reading for the i'th filling of the cuvette determined:

$$\overline{T}_i = \frac{\sum_j^n T_j}{n} \tag{21}$$

and the mean dispersion for a single reading calculated

$$s^2_{T_{sp'}} = \frac{\sum_i^m \sum_j^n (T_j - \overline{T}_i)^2}{m(n-1)}. \tag{22}$$

The dispersion of the mean reading which is determined by the instrumental error is n times less:

$$s^2_{T_{sp}} = \frac{s^2_{T_{sp'}}}{n}. \tag{23}$$

Next, the mean reading of the transmittance scale for a given solution was calculated

$$T = \frac{\sum_i^m \overline{T}_i}{m} \tag{24}$$

and the dispersion of the mean reading determined

$$s_T^2 = \frac{\sum_l^m (\overline{T}_l - T)^2}{m-1}. \qquad (25)$$

The second series of measurements was then checked by the same scheme and the corresponding dispersions found.

The use of Cochrane's G criterion ([11] p. 328) (for a significance level of 0.05) showed that the empirical dispersions in both series are estimates of the same general dispersions.

Dispersion of the Measurement Errors

Readings of the transmittance scale	0,99	0,77	0,58	0,40	0,23	0,13
$\sigma_T^2 \cdot 10^6$	25,2	8,4	17,6	5,9	2,0	3,4
$\sigma_{T_{sp.}}^2 \cdot 10^6$	2,2	2,0	2,1	1,7	0,7	1,5
$\sigma_{T_{gk}}^2 \cdot 10^6$	23,0	6,4	15,5	4,2	1,3	1,9
$\sigma_{T_{cuv.}}^2 \cdot 10^6$	23,3	10,9	47,0	26,2	26,0	105,5*

*Not taken into account during meaning.

In the table is given the mean dispersions for both (k = 2) series for each spectrophotometer reading.

The dispersions s_T^2 and $s_{T_{sp.}}^2$ for each reading T have the following numbers of degree of freedom, respectively, $N_1 = k(m-1) = 6$ and $N_2 = km(n-1) = 16$. For all readings T, apart from T = 0.13, the ratio $s_T^2/s_{T_{sp.}}^2$ exceeds the tabular value of the F-criterion for a significance level of 0.05. At high values of T (0.99; 0.77; 0.58) $s_T^2/s_{T_{sp.}}^2$ exceeds even the value of the F-criterion for a significance level of 0.01.

Accordingly, it can be affirmed that, at least for high values of T, changing the solution introduces a considerable error into the mean reading. This is the cuvette error $\sigma_{T_{gk}}$.

The general dispersions are evaluated empirically as follows:

$$\sigma_T^2 \simeq s_T^2,\ \sigma_{T_{sp}}^2 \simeq s_{T_{sp}}^2 \text{ и } \sigma_{T_{gk}}^2 = \sigma_T^2 - \sigma_{T_{sp}}^2 \qquad (26)$$

Thus, the reality of the existence of the cuvette error is established.

The use of Cochrane's criterion (for a significance level of 0.05) ([11] p. 238) shows that $s_{T_{sp.}}^2$ obtained at various values of T are estimates of the same general dispersion $\sigma_{T_{sp.}}^2$.

Thus, the instrumental error can be regarded as being independent of the spectrophotometer reading. The mean dispersion of the instrumental error $\sigma_{T_{sp.}}^2 = 1.7 \times 10^{-6}$.

Equation (19) shows that there should be a linear relationship between σ_T^2 and T^2. The correlation coefficient of σ_T^2 and T^2 ([12], p. 79), was calculated; r = 0.851 for four degrees of freedom, which exceeds the value of the correlation coefficient for a significance level of 0.05. This indicates that there is a relationship between σ_T^2 and T^2. The equation for the regression line ([12], p. 81) was found in the form

$$\sigma_T^2 = 2{,}9 \cdot 10^{-6} + 20{,}8 \cdot 10^{-6} \cdot T^2. \qquad (27)$$

Equation (27) shows that the equation theoretically derived for the error in measuring the readings of the transmittance scale (19) is applicable to the experimental results.

From a comparison of equations (19) and (27) it follows that the coefficients for the equation of the regression line should be considered as $\sigma^2_{T_{sp.}} = 2.9 \times 10^{-6}$ and $\sigma^2_{T_{cuv.}} = 20.8 \times 10^{-6}$.

We found the dispersion of the transmittance of the cuvette with the blank solution directly from our results:

$$\sigma^2_{T_{cuv}} = \frac{\sigma^2_{T_{gk}}}{T^2} \tag{28}$$

From the corresponding dispersions we find the mean square errors $\sigma_{T_{sp.}} = \sqrt{1.7 \cdot 10^{-6}} = 0.13\%$, $\sigma_{T_{cuv.}} = \sqrt{26.7 \cdot 10^{-6}} = 0.52\%$.

Thus, we find that for a fairly high spectrophotometer sensitivity, $\sigma_{T_{cuv.}}$ is considerably (four times) greater than $\sigma_{T_{sp.}}$, i.e., the precision of spectrophotometric analysis is limited by the cuvette error (when the readings of the spectrophotometer D are not very high).

Accordingly, serious attention must be given to the problem of cutting down the cuvette error, thus: a) it is essential to place the cuvette in exactly the same position each time (by means of a special holder) on the same side of the photoelement; b) on changing the solutions the outer optical surfaces of the cuvette should remain clean so that it should not necessary to rinse and wash them (in the course of a given series of measurements of the optical density of samples and standards).

As we have shown [13], an estimate of $\sigma_{T_{sp.}}$ and $\sigma_{T_{cuv.}}$ is necessary in order to determine the optimum scale readings. The most convenient and suitable method of determining $\sigma_{T_{sp.}}$ and $\sigma_{T_{cuv.}}$ is an m-fold (m = 10-20 changes of solution) photometric measurement of the blank solution with n unit readings for each change of solution (n = 3). The dispersion of the errors are determined according to formulas (21-26) and (28).

The values we obtained for the errors of measurement cannot be regarded as constants. For example, in one of the determinations of titanium by a differential method (on another SF-4 spectrophotometer) the following values were obtained $\sigma_{T_{sp.}} = 0.04\%$ and $\sigma_{T_{cuv.}} = 0.19\%$ ($\sigma_{T_{cuv.}} / \sigma_{T_{sp.}} = 4.8$). From Bastian's results [14] it follows that in his work the ratio $\sigma_{T_{cuv.}} / \sigma_{T_{sp.}}$ is considerably greater than in our experiments (as a result of a smaller instrumental error).

It must be emphasized that in spectrophotometric work, e.g., [7, 15], the reproducibility of spectrophotometer readings, as a rule, was determined by changing the solutions in the cuvettes several times i.e., an error which includes both the instrumental and the cuvette error was calculated. The cuvette error was not analyzed. Nevertheless, in the literature, as we have noted already, it is always stated that the error in the readings of the transmittance scale is constant. Thus, the constancy of the instrumental error has been extended without any proof to the cuvette error. As pointed out in the present article, this contradicts both theoretical and experimental results.

Limiting (Boundary)-Reading

The equations for the total error in the spectrophotometer readings testify to the fact that when $\sigma_{T_{sp}} < \sigma_{T_{cuv.}}$ (which is usually the case in practice) then at low values of D (high T), the error is determined by the reproducibility of the state of the cuvette (Fig. 1 and 2). On the other hand, for fairly large values of D (small T) the error in the spectrophotometer readings is determined by the instrumental error.

There exists a definite limiting (boundary) value for the scale reading for which both components are equal:

$$\sigma_{T_{gk}} = T \sigma_{T_{cuv}} = \sigma_{T_{sp}}$$

From which

$$T_{\text{lim}} = \frac{\sigma_{T_{sp}}}{\sigma_{T_{cuv}}}.$$

It should be remembered that $\sigma_{T_{sp.}}$ is the instrumental error of the mean reading, which depends on the number n of repeated individual readings.

For a given analysis (constant sensitivity of the spectro photometer, the same number of individual readings, and the same method of treating the cuvette) the limiting reading of the scale is constant.

Introducing the limiting reading of the scale into the equation for the errors of the spectrophotometer readings, we get:

$$\sigma_D = \sigma_{D_{cu}} \sqrt{1 + \left(\frac{T_{\text{lim}}}{T}\right)^2}, \tag{31}$$

$$\sigma_T = \sigma_{T_{cuv}} \sqrt{T_{\text{lim}}^2 + T^2}, \tag{32}$$

$$\sigma_D = 0{,}43\sigma_{T_{sp}} \sqrt{\frac{1}{T_{\text{lim}}^2} + \frac{1}{T^2}}, \tag{33}$$

$$\sigma_T = \sigma_{T_{sp}} \sqrt{1 + \left(\frac{T}{T_{\text{lim}}}\right)^2}. \tag{34}$$

For $\sigma_{T_{cuv.}} = 0$, and consequently $T_{\text{limit.}} = \infty$, equations (33) and (34) transform into the well known equations

$$\sigma_D = \frac{0{,}43\sigma_{T_{sp}}}{T}, \tag{35}$$

$$\sigma_T = \sigma_{T_{sp}} = \text{const.} \tag{36}$$

But, as already pointed out, usually $T_{\text{limit.}} = \sigma_{T_{sp.}} / \sigma_{T_{cuv.}} < 1$. It can be shown that only for $T \leq 0.46\ T_{\text{limit.}}$, i.e., only for very small T (very large D), is $\sigma T = \sigma_{T_{sp.}}$ (with an accuracy of up to 10%) and it can be considered that σ_T = const.

Thus, under normal analytical conditions, i.e., for not very large D, the error in measuring the reading of the transmittance scale cannot be regarded as being independent of the readings. At low D ($T \geq 2.2\ T_{\text{limit.}}$) the error in measuring the reading of the optical density scale can be regarded as constant: $\sigma_D = \sigma_{D_{cuv.}}$ = const. (with an accuracy of up to 10%).

SUMMARY

The sources of random errors in measurements carried out on an electrically compensated spectrophotometer are considered.

An equation is derived for the errors in spectrophotometric measurements, taking into account the non-reproducibility of the state of the cuvette (purity and position). It has been established that the error in measuring the readings of the transmittance scale depends on the value of the reading.

A study has been made of the reproducibility of measurements carried out on an SF-4 spectrophotometer. It has been shown that the decisive factor affecting the precision of the measurements when using a highly sensitive spectrophotometer is the nonreproducibility of the state of the cuvette.

The equation derived for the errors in measurement has been verified experimentally.

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A STUDY OF THE ERRORS OF X-RAY SPECTROGRAPHIC ANALYSIS

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At present a number of papers are being published on the application of the methods of mathematical statistics for studying the various problems of analytical chemistry [1-6]. The aim of the present work was the use of these methods for a comparative study of the errors of x-ray spectrographic analysis. The study was carried out taking as an example the quantitative x-ray spectrographic determination of Hf and Zr in menerals and the products of technological treatment.

Apparatus and Experimental Procedure

For our work we used a vacuum focusing x-ray spectrograph of the Johann type with an x-ray tube fitted with a tetrahedral anode [7] and operating on the flyback principle [8]. The tetrahedral anode of the x-ray tube could be rotated on a joint around its axis without breaking the vacuum. In order to cut down the background, the anode was made from aluminum. Under the operating conditions of 25 kilowatts, 6 ma, and a 15 minute exposure, the sensitivity for the determination of Hf was 0.01%. For the determination of more than 0.1% and 5% of Hf and Zr respectively, exposure time could be reduced to 6 minutes without any sacrifice of accuracy. A bent quartz crystal with reflecting surfaces ($11\bar{2}0$) was used. The radius of curvature of the crystal was 500 mm. Zr and Hf were determined quantitatively on the basis of the $K\beta_1$ and $L\beta_1$ lines of these elements respectively in the second and first order of reflection. The technique used in this work differed in this particular respect from that described previously [7]. In order to avoid distortion of the relative intensity of the lines of both elements (the determination of which is of special interest for carrying out geochemical studies), the crystal plus casette was uniformly rocked within the limits of the angles of reflection from 15°30' to 17°. The spectra from the sample located on the four faces of the multifaced anode were recorded on one film. For this purpose, in front of the focal circumference of the casette was fixed a shutter with a slit through which only a fine beam of x-rays containing the β_1 lines of the test elements and the narrow adjoining part of the spectrum could pass. The film was pulled behind the slit in the shutter by means of a SD-2 synchronous motor after expiration of the chosen exposure time.

The cathode of the x-ray tube was provided with a focusing hood in the form of a brass square 10 × 10 mm. Inside the latter were placed two quartz rods with platinum wire 0.5 mm in diameter and 120 mm long wound on them; the wire was covered with an oxide paste of the usual composition. The oxide layer was not renewed more often than after 60-70 hours of operation of the x-ray tube. When the cathode was constructed in this way, the focusing spot was almost a right rectangle with an area of 2 × 3 mm.

The current passed through the x-ray tube was kept constant (with an accuracy of ± 0.5%) by means of a special stabilizer. The high voltage was supplied to the tube from a double semiperiod transformer. The voltage was kept constant by means of a S-96 kilovoltmeter. The vacuum in the apparatus ($2.5\text{-}6 \times 10^{-2}$ mm Hg) and in the x-ray tube ($5\text{-}6 \times 10^{-5}$ mm Hg) was also kept constant, as well as the distance between the anode and the cathode h, and the filament current of the cathode $i_{cath.}$. The spectrograph case was separated from the x-ray tube. The vacuum was measured separately in the two parts.

The use of aluminum anodes necessitated a change in the method of placing the samples on them. Instead of the usual technique of rubbing the sample into the surface of the anode, the following technique was used. The anode was treated with emery (corundum) paper until an even, roughened surface was obtained. 1-2 mg of test

material was then uniformly spread on the anode surface by means of a razor blade, and, using the same razor blade the surface was then covered with a thin layer of BF-2 paste. During the preaging of the tubes, before an actual determination, the solvent in the paste evaporates away while the sample on the anode remains covered with a thin film, and, as tests showed, is kept stably in such a position for many hours. The more effective use of the sample, which is ensured by adopting such a technique for applying it to the anode, increases the intensity of the spectral line by approximately 30%. Another advantage of the method (compared with the rubbing technique) is the high degree of uniformity of the layer formed on the anode.

Standards were prepared by careful mechanical grinding of weighed amounts of zirconium and hafnium oxides with the titanium oxide used as a base. The standards contained 0.25, 0.5, 1.0, and 2.5% of hafnium and 20% of zirconium, and were similar in composition to the minerals or rock concentrates which are met in the course of geochemical studies.

Each of the standards was placed on one of the faces of the anode, and, after preaging, was x-rayed under strictly standard conditions; the process was repeated a number of times, and after definite time intervals, on one film. Duro-film was used. Development was carried out in cylindrical tubes, in fresh standard "Rapid" developer for 18 minutes at 18 ± 0.5° in a thermostat. Four spectrograms 15 × 150 mm were developed in each tube. The films were fixed in an acid fixer.

The spectrograms were photometrically measured on a MF-2 photometer with a slit of 130 and a logarithmic scale, all the lines being measured at the same height (1 mm from the lower edge of the spectrum). The blackening of the spectrogram background ($S_{back.}$) was measured on one side of the line, since interfering lines were located on the other side. The line blackening S_1 was calculated by means of the formula $S_1 = \Delta S = S_{1\,+\,back.} - S_{back.}$.

A Statistical Study of the Errors of Quantitative X-Ray Spectrographic Determination of Hf and Zr

The first step in our studies was to verify the hypothesis of normality.* A normal distribution of the analytical results, as one would expect on the basis of the limiting theorem of Lyapunov, should be obtained in those cases where there are no dominating factors among the numerous factors affecting the experimental results. In order to check the normality hypothesis, in analytical practice one often makes a statistical analysis of the results of multiple measurements of the same magnitude. Nevertheless this is not the best method, since the results of such an experiment may be affected by factors which slowly change with time, leading thereby to a shift in the scatter center. Under such conditions, the normality hypothesis may be rejected because of incorrect planning of the experiment. More reliable results can be obtained by a combination of small selections [9-11], where instead of studying the distribution of the random value χ, the law of the distribution of the relative deviation** $\tau = \frac{x_i - \bar{x}}{s\sqrt{\frac{n-1}{n}}}$, is studied. When such a method is used, both the distribution parameters—the mean and dispersion—

may have different values for different selections. The theoretical values of the frequencies of the τ-distribution are tabulated in [9]. 216 measurements were used (72 selections, each of which consisted of three determinations). The results are presented in Table 1. The group interval is given in the first column, while the second column contains the theoretically expected absolute frequency ν_i^0 of the appearance of the value τ included in the limits of the interval indicated; the third column contains the frequency actually observed ν_i. Finally, the last column of the Table contains the calculated weighed sum of squares for each of the series of independent determinations $\chi^2 = \sum \frac{(\nu_i - \nu_i^0)^2}{\nu_i^0}$, these are compared with the tabulated values of the χ^2 distribution [10]. As is evident,

$P(\chi^2 > \chi^2_{expt.}) = 0.3$, which therefore confirms the normality hypothesis.

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*During the application of mathematical statistics to new test materials it is always advisable to start with verication of the hypothesis of normality; this facilitates further statistical analysis.

** In this article, in accordance with accepted tradition, S^2 denotes the selected dispersion and σ^2 the general dispersion.

TABLE 1

Checking the Normality Hypothesis for Reproducibility Errors

Group intervals		Theoretically expected freq. accord. to [9] (ν_i^0)	Freq. observed experimentally (ν_i)	$(\nu_i - \nu_i^0)^2/\nu_i^0$
Positive deviations	0,0—0,3	4,90	5	0,002
	0,3—0,6	5,16	6	0,144
	0,6—0,9	5,76	9	1,823
	0,9—1,2	7,41	7	0,022
	1,2—1,5	12,79	18	2,122
Negative deviations	0,0—0,3	4,90	6	0,246
	0,3—0,6	5,16	5	0,004
	0,6—0,9	5,76	5	0,100
	0,9—1,2	7,41	1	5,520
	1,2—1,5	12,79	10	0,605
	Sum	72	72	10,588

Note: The number of degrees of freedom f = 10-1 = 9, $P(\chi^2 > \chi^2_{expt.}) \simeq 0.3$.

The verification of the normality hypothesis described, only relates to intralaboratory reproducibility errors. It was also of interest to check this hypothesis for errors characterizing the deviation between the results of determinations obtained by chemical and spectrographic methods. For this purpose we treated the results of 48 parallel chemical and x-ray spectrographic determinations. The results are illustrated in Table 2. The first column contains the group intervals expressed in parts of σ; the second column contains the absolute frequency expected on the basis of a normal distribution (ν_i^0); while the last column contains the experimentally observed frequencies (ν_i), and the values of $(\nu_i - \nu_i^0)^2/\nu_i^0$ calculated for them. A comparison of the experimental results with the theoretically calculated frequencies indicates that the distribution studied is near to normal. The fact that the normality hypothesis is valid allows one to use analysis of variance for investigating the errors of x-ray spectrographic determinations. In the first instance it is reasonable to resolve the total experimental error into two values; the reproducibility error $\sigma_{reprod.}$ characterizing the scatter of the experimental results with respect to the mean obtained during a short time interval, and σ_T the error determined by other factors. For this purpose the results of 20 determinations for each of four standards (three in parallel) were treated; all were taken on one plate. The results of the experiments for each of the standards were arranged as shown in Table 3. Here the scatter along

TABLE 2

Verification of the Normality Hypothesis for Errors Characterizing the Deviation between the Results of X-Ray Spectrographic and Chemical Analysis

Group intervals	Theoretically expected frequency ν_i^0	Experimentally observed frequency ν_i	$(\nu_i - \nu_i^0)^2/\nu_i^0$
0.0-0.67	23.8	27	0.43
0.67-1.0	8.8	6	0.89
1.0-1.4	7.5	6	0.30
1.4-2.0	7.9	9	0.15
Sum	48	48	1.77

Note: The number of degrees of freedom f = 4-2 = 2; $P(\chi^2 > \chi^2_{expt.}) \simeq 0.4$.

TABLE 3

Arrangement of Material during a Study of the Dispersion Determined by the Effect of One Factor

Parallel determinations	Films		
	1	2 . . .	20
First	x_{11}	x_{21}	x_{201}
Second	x_{12}	x_{22}	x_{202}
Third	x_{13}	x_{23}	x_{203}

the columns is determined by the reproducibility error $\sigma_{reprod.}$ in experiments separated by small time intervals, while the vacuum of the apparatus remains unchanged, and the apparatus works under constant conditions and the same conditions are used for developing the spectrograms; $\sigma_{reprod.}$ does not depend on the conditions used for securing the sample to the anode of the x-ray tube. The factors which have the greatest effect on this error are the nonuniformity of the focusing spot, and the extent of its shift along the anode surface with an unevenly deposited sample, and also errors introduced into the experimental results during photometric determinations of the spectrograms. The scatter between the columns σ_T in Table 3 is caused by other factors. It may depend on errors arising because of some variation in the vacuum and on other parameters which affect the operation of the spectrograph, and on imperfections and differences in the conditions of attaching the test material to the anode of the x-ray tube and on differences in the conditions under which the spectrograms are developed. The dispersion was calculated by means of well known formulas [5]; results of these calculations are given in Table 4. It was established that $\sigma_{reprod.}$ and σ_T depend on the concentration of the test element (Figs. 1 and 2).

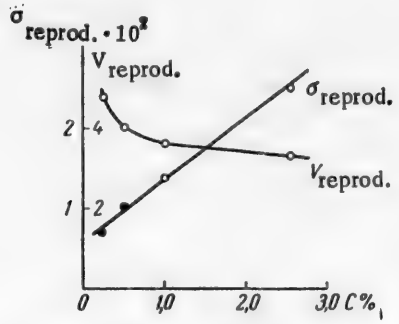

Fig. 1. Relations between the values of $\sigma_{reprod.}$ (1) and $v_{reprod.}$ (2) and the concentration of the test element.

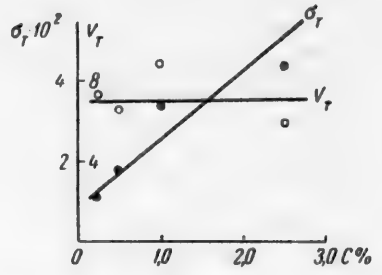

Fig. 2. Relations between the values of σ_T (1) and v_T and the concentration of the test element.

As for the variation coefficients V_{VT} and V_{VT} (the relative errors of the measurements), in view of the fact that for x-ray spectrographic determinations the following relation holds

$$\log \Delta S = a + b \log C$$

these can be calculated by means of the formula

$$v = \frac{\sigma_c}{C}\% = \frac{\sigma_{\Delta S}}{b \cdot \Delta S} \cdot 100,$$

they are almost constant for all the tested range of changes in concentration of the elements, and are equal, on an average, to 3.9 and 7.1% respectively (Table 4).

TABLE 4

The Square Errors and Variation Coefficients during Hafnium Determination

C, %	$\overline{\Delta S}$	$\sigma_{reprod.} \times 10^2$	$\sigma_T \cdot 10^2$	$V_{reprod.}$ %	V_T, %
0.25	0.123	0.71	1.09	4.7	7.2
0.50	0.225	1.02	1.69	4.0	6.6
1.00	0.334	1.37	3.36	3.6	8.8
2.50	0.652	2.47	4.36	3.3	5.9

An attempt was made to resolve the error σ_T into two values: σ_{RT}, the error determined by the instability of the processes of rubbing the standard on the anode and $\sigma_{T'}$, the error determined by the remaining factors which are not controlled and which change slowly with time. Experiments were carried out so that four standards containing the same amount of Zr were rubbed into the four different faces of the anode. 12 spectra were photographed on each film (4 standards in triplicate). In the course of 1.5 months 20 films were prepared containing 240 spectrograms altogether. The experimental results were presented in the form of a two stage group as shown in Table 5. Analysis of variance* showed (Table 6) that σ_{RT} and $\sigma_{T'}$ differ significantly from zero. Calculations led to the following results.

$$\sigma_{rep} = 1{,}05 \cdot 10^{-2} \quad V_{rep} = 3{,}2\%$$
$$\sigma_{RT} = 1{,}53 \cdot 10^{-2} \quad V_{RT} = 4{,}6\,,$$
$$\sigma_{T'} = 2{,}02 \cdot 10^{-2} \quad V_{T'} = 6{,}1\,.$$

TABLE 5

Arrangement of Material During a Study of Dispersion Determined by the Action of Two Factors

Parallel determinations	Plates		
	1 . . . 20		
	Rubbing 1 . . . 4	. . . . .	Rubbing 1 . . . 4
First	$x_{111} \ldots x_{141}$	. . . . .	$x_{2011} \ldots x_{2041}$
Second	$x_{112} \ldots x_{142}$	. . . . .	$x_{2012} \ldots x_{2042}$
Third	$x_{113} \ldots x_{143}$	. . . . .	$x_{2013} \ldots x_{2043}$

Thus, the results of an analysis of variance show that in the general balance of errors, in addition to the rubbing process (which obviously needs improving) other uncontrolled factors play a large part. In this connection there arises the necessity of clarifying the question of the expediency of increasing the number of controlled factors, and applying the necessary corrections for such factors.

First, attention was given to the development process. Variations in the temperature and duration of the development of the spectrograms (using a standard developer) have an appreciable affect on the position of the calibration curves. For example, on changing the duration of development (Fig. 3) there is observed a parallel shift of the curves. This is reflected in the absence of correlation between the values X and Y (Fig. 4)

*For a detailed description of the analysis of variance for a two stage classification see, e.g., [12].

determined by the method of least squares in the equation

$$\Delta S = X + YC,$$

by means of which it is possible to represent (Fig. 3, below) the relation between the blackening of the x-ray lines of hafnium and its concentration in a sample for a narrow concentration range.

TABLE 6

Results of Analysis of Variance Obtained during a Study of Errors Arising during Determination of Zirconium

Origin of the dispersion	No. of degrees of freedom	Sum of squares	Mean sum of squares	F
Plates obtained at different times (factors which change slowly with time)	20-1 = 19	788.15	41.48	3.1*
Rubbing	20 (4-1) = 60	799.83	13.33	12.1**
Reproducibility	80(3-1) = 160	176	1.10	—
Sum	239	—	—	—

*Significant for a significance level of 0.001

** The same for << 0.001.

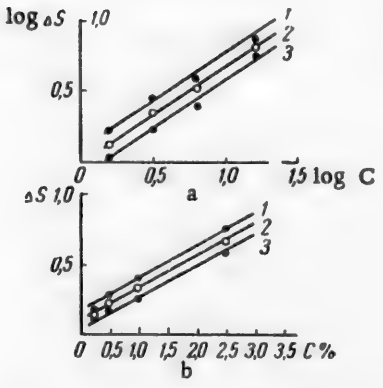

Fig. 3. Calibration curves for the x-ray spectrographic determination of Hf in a sample, and the relation between their position and the duration of development 1) 10 minutes; 2) 8 minutes; 3) 6 minutes.

Neither was any correlation established between the values of X and Y and changes in the most important parameters characterizing the conditions under which the spectrograph operates—the strength of the filament current $i_{cath.}$, the pressure p in the apparatus, and the distance h between anode and cathode. The results given graphically in Figs. 5-9 testify to this. Worthy of attention is the fact that the parameter X (Fig. 5a, 6a, 7, 8, and 9) varies within fairly wide limits (from 0.07 to 0.14), while the slope of the calibration curve—parameter Y (Fig. 5b, 6b, 7, 8, 9) remains almost unchanged (about 1.13).

Thus, it seems that there is no need to apply corrections for changes in the filament current, and for changes in the pressure, and the distance between the anode and cathode. At the same time there occurs a parallel shift in the calibration curves, which is, presumably, caused by some instability in the development process. From a practical point of view it must be acknowledged that it is necessary to use one standard for controlling the position of the calibration curve, although this precaution leads to an increase in the duration of a determination.

The precision of the determination of the mean value $\overline{\Delta S}$ both for the control standard, and for the test sample is calculated by the formula:

$$\sigma_{\overline{\Delta S}} = \sqrt{\sigma_r^2/nm + \sigma_{rt}^2/m},$$

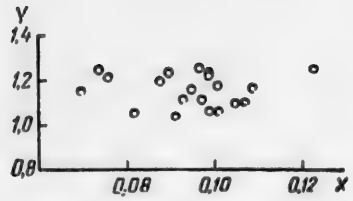

Fig. 4. Verification of the hypothesis regarding the correlation between the parameters of the calibration curve.

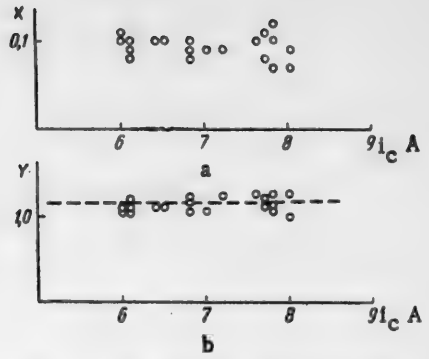

Fig. 5. Verification of the hypothesis of a link between parameters X (a) and Y (b) and changes in the filament current of the cathode $i_{cath.}$

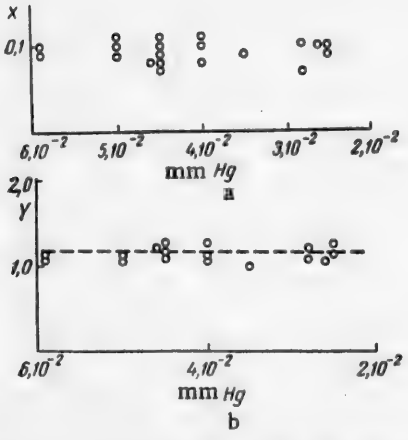

Fig. 6. Verification of the hypothesis of a relation between the parameters X (a) and Y (b) and changes in the vacuum of the spectrograph.

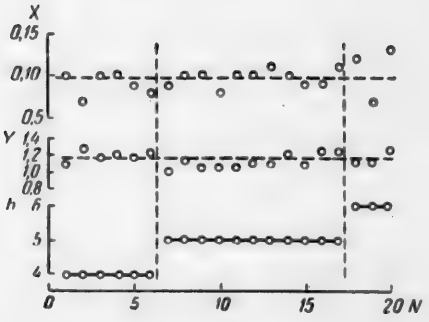

Fig. 7. Change in the parameters X and Y with time for three varying distances h between the anode and the cathode in the x-ray tube.

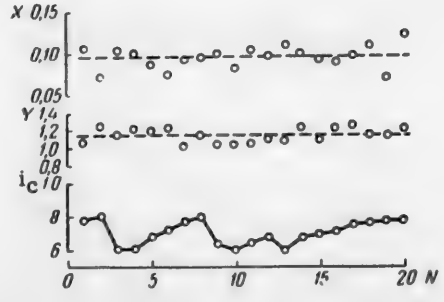

Fig. 8. Verification of the hypothesis of a relation between the parameters X and Y and changes in the strength of the filament current of the cathode with time.

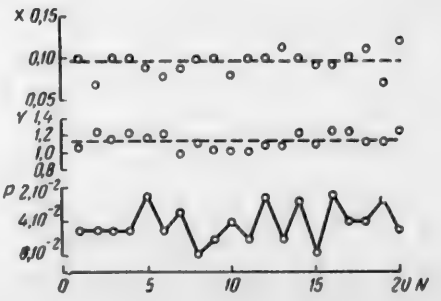

Fig. 9. Verification of the hypothesis of a relation between the parameters X and Y and changes in the vacuum in the spectrograph with time.

TABLE 7

The Relation between the Errors in Determining $\overline{\Delta S}$ and the Amount of Rubbing and the Number of Parallel Determinations

m	n	$\sigma_{\overline{\Delta S}} \cdot 10^{-2}$
1	1	1.85
1	2	1.70
1	3	1.65
2	1	1.51
2	2	1.31
2	3	1.24

where m is the number of parallel rubbings (applications), and n is the number of parallel determinations for each rubbing. In Table 7 are given the results of calculating $\sigma_{\overline{\Delta s}}$ for various values of m and n. The numbers obtained show that on using a tetrahedral anode, the optimum precision is obtained for m = 2, n = 2* when it is necessaery to photograph the standard and sample simultaneously. When m = 1, changing from n = 2 to n =3 has almost no effect on increasing the precision of the determination of the mean value S.

It is necessary to pay attention to the essential difference between x-ray spectrographic and emission optical methods of analysis. For an optical method, in the general case, it is necessary to take into account changes in both the parameters X and Y of the curves. The values of $\sigma_{reprod.}$ and σ_T in an optical spectrographic method, in contrast to the x-ray spectrographic method, do not depend on the concentration of the test component.

SUMMARY

Taking as an example the quantitative x-ray spectrographic determination of zirconium and hafnium in minerals and rocks, an analysis of variance of the errors has been made. The role of various factors which affect the precision of the determination of the elements has been evaluated quantitatively. A study has been made of the correlation between the parameters of the calibration curves and changes in the conditions under which the analysis is conducted and the conditions used for developing the spectrograms. It has been shown that, in contrast to optical spectrographic analysis, for which, in the general case, it is necessary to take into account changes with time of both parameters of the calibration curve, in the case of x-ray spectrographic analysis only mutual parallel displacement of the curves occurs. This makes it possible to carry out a determination on the basis of one constant calibration curve, the position of the latter being controlled by means of only one standard with not a very small content of the test element. For known values of $\sigma_{reprod.}$, σ_{RT}, and σ_T' the basic curve should only be shifted in that case where the position of the points corresponding to the control standard is shifted from the curve by a distance exceeding $\pm 2\sqrt{\frac{\sigma_r^2}{nm} + \frac{\sigma_{rt}^2}{m}}$ (where m is the number of parallel rubbings, and n is the number of parallel determinations for each rubbing). When this shift lies outside the limits of $\pm 2\sqrt{\frac{\sigma_r^2}{nm} + \frac{\sigma_{rt}^2}{m} + \sigma_{T'}^2}$, the experimental results should be regarded as incorrect and should be repeated. When a tetrahedral anode is used in order to increase the accuracy, it is best to choose m = 2, n = 2 for the determination, both for the test material and the control standard.

When one constant calibration curve is used for carrying out express determinations without a control standard, increasing the number of photographs for one rubbing should have little effect on the experimental

*Even greater possibilities are opened up by further increasing the number of faces on the anode.

results, since its error to a large extent depends on the value of $\sigma^2_{RT}+\sigma^2_{T'}$, which does not decrease under these conditions. It should also be borne in mind that the experimental precision obtained when a constant calibration curve is used, which has been obtained by meaning experimental results on different plates and at different times, cannot be increased by periodically checking the calibration curve. This can only be achieved by taking spectrograms on the same plate as that used for the control standard.

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THERMOSPECTROPHOTOMETRIC DETERMINATION OF THE RARE EARTH ELEMENTS IN THE PRESENCE OF THORIUM

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The photometric determination of thorium in fairly acid solutions against a background of the rare earths can be carried out without any difficulty. Determination of the rare earths in the presence of thorium is, however, difficult. It is necessary, first of all, to separate thorium, using well known techniques [1-9], or to carry out two determinations of the light absorption at different pH values and determine the rare earths by difference [6, 10]. The latter method has, of course, limited application, and for low rare earth contents gives inaccurate results, or may be inapplicable altogether.* As far as we are aware there are no direct chemical methods for the determination of the rare earths against a background of thorium. Such determinations become possible on using a new technique which we have called thermophotometry.

By thermophotometry or thermospectrophotometry we designate the technique whereby spectrophotometric determinations are carried out at two different temperatures. If the solution contains only two elements, and if, on changing the temperature, the light absorption of the complexes of these elements changes to a different extent, then having obtained two values of the optical density at the different temperatures, the content of each element can be determined by solving a system of two simultaneous equations with two unknowns. In individual cases this general method can be essentially simplified. The essence of this phenomenon has already been described earlier [11].

The effect of pH on the intensity of the color of solutions of the complex compounds formed by reagents of the type R-OH, is shown in the general form in Fig. 1. Curves of this type are observed for all temperatures. Under such conditions, the higher the temperature, the more is the curve displaced to the acid side**. The decrease in the color intensity on increasing the pH to a value greater than that corresponding to maximum development of the color, is probably connected not with decomposition of the complexes as is sometimes assumed, but with a decrease in the intermolecular dissociation of these cyclic complexes, which is also responsible for the colors observed [12]. On heating a solution of the complex having a pH lying on the ascending branch of the curve (Fig. 1, a), the color intensity of the solution will increase. When the pH corresponds to a point lying on the descending branch of the curve (Fig. 1, b), the color intensity, will on the other hand, in hot solutions be lower than in cold solutions. At a pH corresponding to the point of intersection of the curves (Fig. 1, c) the intensity of the color of a solution of the complex (but not the intensity of the color of excess colored reagent present) will be the same at those temperatures for which the curves were constructed. At other temperatures the curves will intersect at another point.

*The possibility is indicated in the article by Kuteinikov and Lansky [10] of photometric determinations of the rare earths on a background of thorium by difference. However, these authors do not give details of a method or of any results they may have obtained.

**As a consequence of additional reasons not considered here, the descending branch of the curve corresponding to the higher temperature is not always shown up so clearly and correctly as shown in Fig. 1.

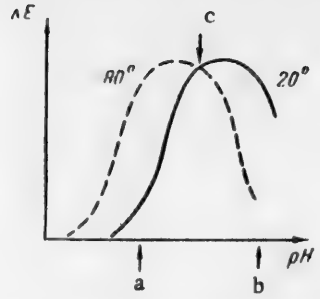


Fig. 1. Relation between the light absorption of a solution of the complex an and pH at 20 and 80° (scheme)

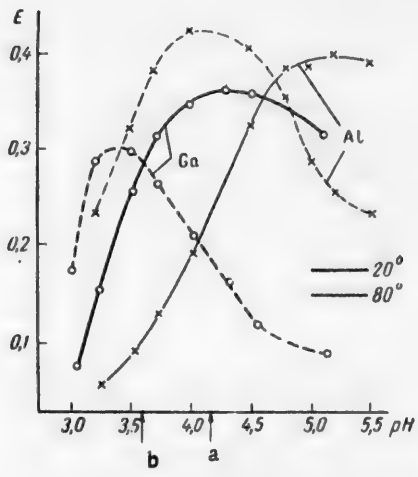


Fig. 2. Effect of temperature on the light absorption of solutions of the complexes of Al and Ga with arsenazo on changing the pH. Concentrations in mole liter; Al 0.00025; Ga 0.00050; arsenazo 0.00050. Cuvette length 40 mm. λ = 576 mμ.

When the cations of two elements which hydrolyze with varying ease are present in solution, the optimum conditions for color development of their complexes will be found at different pH. On comparing the curves for two elements, as is shown for the case of compounds of Al and Ga with arsenazo in Fig. 2, it is clear that at the pH corresponding to point a, heating will increase the intensity of the color of the Al complex and simultaneously weaken the intensity of the color of the Ga complex. At a pH corresponding to point b, the increase in the color intensity will be proportional to the concentration of the Al complex, since the intensity of the color of the Ga complex at this pH will not change with changes in temperature.

The same is true of a mixture of two other cations which hydrolyze at different pH's, i.e., cations whose hydrocomplexes of the type $Me(OH)^{n+}$ have different instability constants. The values of these constants can be found in the monograph by Yatsimirsky and Vasil'ev [13].

If it were necessary to determine an element with readily hydrolyzable cations on the background of an element with cations which hydrolyze with difficulty, e.g., Th on a background of La, such a determination could be carried out without any difficulty. It is simply necessary to work at as low a pH as possible when the element whose cations hydrolyze with difficulty does not react. Thermophotometry is also interesting in that it permits solution of problems which the techniques of ordinary photometry cannot solve. For example, it is possible to determine In on a background of Ga, although Ga^{3+} cations hydrolyze more readily than In^{3+}. Similarly, it is possible to determine Al on a background of In, Al on a background of Ga, etc. Arsenazo (benzene-2-arsonic acid -< 1-azo-7> > -1, 8-dihydroxynaphthalene-3, 6- disulfonic acid) is suitable for this purpose. For determination of Al on a background of Th, the reagent benzene-4-sulfonic acid < 1-azo-2 > , 1, 8-dihydroxynapthalene-3, 6-disulfonic acid etc., is suitable.

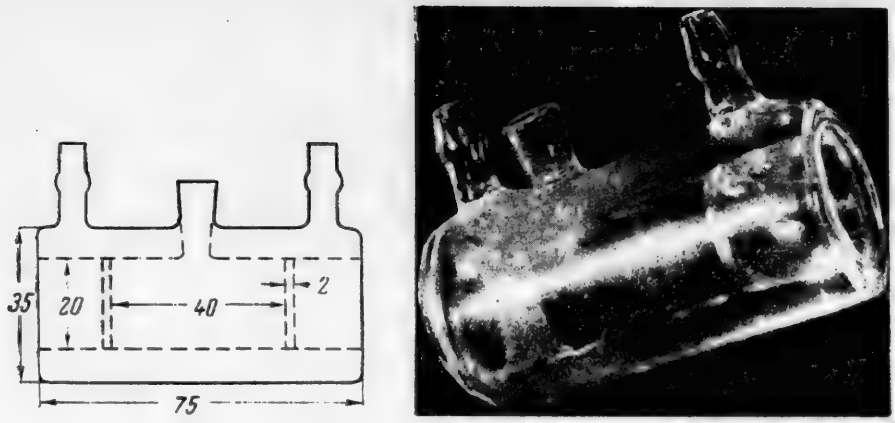
Apparatus

For thermophotometric determinations it is necessary to make measurements of the light absorption at two different temperatures. Of numerous known setups [14-19] which enable the solutions which are being examined to be thermostatted, we chose a quartz cuvette with a jacket (Fig. 3).

A cuvette made from plexiglass can be used. In such a case, however, one cannot work at temperatures higher than 80°. There also arise difficulties associated with getting rid of bubbles of air which adhere to the inner walls of the cuvette during the process of heating the solutions.

Water from Heppler thermostats operating at 20 and 80°, and which can be fairly accurately maintained within ± 0.1-0.2°, is passed into the jacket of the cuvette. Changes in temperature are made by switching over from one thermostat to another by means of taps (screw clips) a and b shown in Fig. 4.

Since the solutions obtained possess too high an optical density, their light absorption should be measured against a grey filter; an uniformly exposed photographic plate with a light absorption of about 3.0 units of optical density is suitable for such a filter.



a b

Fig. 3. Cell fitted with a water jacket

During the experimental work the slit width should be kept constant for construction of the calibration curves and for actual determinations.

Thermospectrophotometric Determination of the Rare Earths in the Presence of Thorium. Arsenazo (benzene-2-arsonic acid-<1-azo-7> -1, 8-dihydroxy naphthalene-3, 6-disulfonic acid) is suitable for this purpose; the color reaction of this reagent with the rare earths [20] and its use for the determination of thorium [21, 22] have been described earlier. Arsenazo solutions are rose in color: with Th and the rare earths it forms soluble complex compounds with a violet color.

In Figs. 5 and 6 is shown the effect of pH on the color intensity of solutions of the complex compounds of thorium and mixtures of the rare earths at 20 and 80°.

On heating the solution from 20 to 80° the color intensity of a solution of the thorium complex at a pH of 3.6-3.8 changes little, while the color intensity of solutions of the rare earth complexes at a pH of 3.7 increases 1.9 times for La, about 2.9 times for Yb, and about 2.9 times* for mixtures with the composition we used.

On adding this mixture of rare earths to thorium nitrate free from rare earths, and working at a pH of 3.7, we constructed a calibration curve (Fig. 7). Then, using this curve, the rare earth content of thorium nitrate to which a mixture of rare earths of the same composition had been added, was determined. The results obtained show clearly (Table 1) how the experimental accuracy can be increased by taking the mean of five determinations.

Experimental Procedure. The method is designed for the analysis of separate mixtures of thorium and rare earths. All other elements apart from the alkali metals should be absent. Masking anions which complex Th and the rare earths should also be absent.

The standard nitric acid solution of the nitrates of the rare earths contains 1.0 mg/liter of total rare earths. The most suitable mixture is one which has a similar composition to the test mixture. In order to prepare it, an accurate aliquot of the calcined oxides (about 0.1 g) is dissolved in HNO_3 and the solution evaporated on a water bath to dryness; the residue is dissolved in water and the volume made up to 100 ml with water. 1.00 ml of this solution is then diluted with water to 100 ml (10 γ /ml of total rare earths).

*A mixture of the rare earths of the yttrium group was used. The composition of the mixture as determined x-ray spectrophotometrically was as follows (% wt.).

Lu 0,75	Ho 1,9	Tb 0,5	Nd 0,9
Yb 6,8	Y 57,0	Gd 1,8	Ge 1,5
Er 7,5	Dy 6,3	Sm 0,3	La 0,75

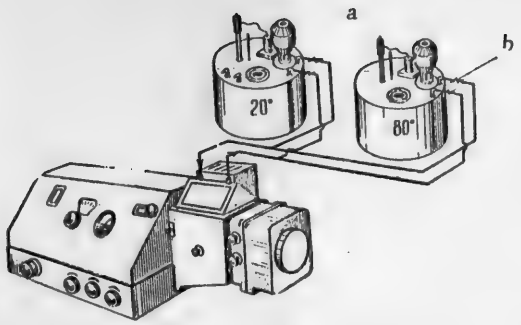


Fig. 4. Schematic diagram of the setup used for thermospectrophotometric determinations.

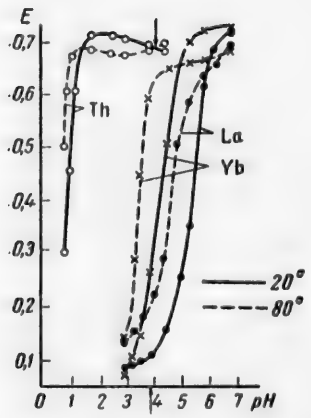


Fig. 5. Effect of temperature on the light absorption of solutions of the complexes of thorium and the rare earths with change in pH. The reagent was arsenazo; λ = 576 mμ; cuvette length 40 mm.

The solution of thorium nitrate in 0.5 N HNO_3 containing about 10 mg/ml of ThO_2 is prepared as follows. About 1 g of $Th(NO_3)_4 \cdot 4H_2O$ free from the rare earths* is dissolved in 50 ml of 0.5 N HNO_3 and the thorium concentration determined gravimetrically.

A buffer solution with a pH of 3.7 is prepared by dissolving 4.72 g of monochloroacetic acid in 10 ml of water and adding, with mixing, in small portions, 21.8 ml of 2.0 N NaOH, and the volume made up to 50 ml. The buffer solution with pH 2.0 is prepared by dissolving 4.72 g of monochloroacetic acid in 10 ml of water and adding, with mixing, 6.12 ml of 2.0 N NaOH and making the solution up to 50 ml.

Construction of a Calibration Curve. Into five 25 ml standard flasks are introduced aliquots of the thorium nitrate solution containing 0.23 mg of ThO_2, and aliquots of the solution of the mixture of rare earths containing 0.000; 0.005, 0.010; 0.020; 0.040 mg of the elements calculated in terms of total oxides; the volume is made up to about 5 ml, and 2 drops of 0.1% phenolphthalein solution added, the mixture is titrated with 0.1 N NaOH until a red color is obtained, the color is destroyed by addition of two drops of 0.05 N HCl. Another 0.016 ml of 0.05 N HCl is added and 8.0 ml of 0.3% aqueous arsenazo solution added, this is followed by addition of 0.4 ml (not more) of the buffer mixture with pH 3.7 and the volume made up to the mark with water. The solutions which are thoroughly mixed are photometrically measured at 20 and 80° in a cuvette with a layer thickness of 40 mm, using a constant slit width of 0.6 mm at a wave length of 576 mμ. The difference between the light absorption of solutions at 80 and 20° is used for constructing the calibration curve.

Analytical Procedure. When solid nitrates or chlorides are analyzed, an aliquot of the preparation corresponding to 10 mg of total oxides of the elements is dissolved in 0.1 N HNO_3 in 100 ml standard flask.

* When the thorium nitrate contains rare earth elements they are removed by extraction of the thorium nitrate with methyl ethyl ketone [6]. To 1 g of thorium nitrate is added 2 ml of concentrated HNO_3 and the mixture dissolved in 50 ml of water. 75 g of solid ammonium nitrate is added and the solution obtained extracted with an equal volume of methyl ethyl ketone. The ketone extract is washed 3 times with half its volume of a 60% solution of ammonium nitrate acidified with nitric acid. The thorium nitrate is reextracted from the separated ketone phase with 50 ml of 0.1 N HNO_3. After the thorium concentration of the reextract has been determined it is used for the work.

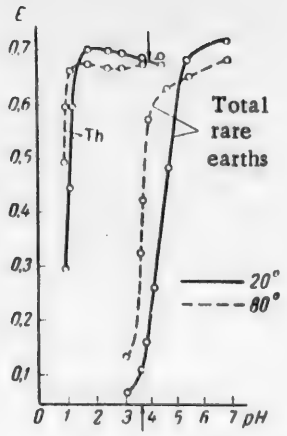


Fig. 6. Effect of temperature on the light absorption of complexes of thorium and the mixture of rare earths used with changes in pH. Reagent—arsenazo; λ = 576 mμ; cuvette length 40 mm. The curves were obtained with solutions of the following concentrations arsenazo 5×10^{-4} mole; Th 1.9×10^{-4} M and a mixture of the rare earths with a concentration of 1.8×10^{-4} M.

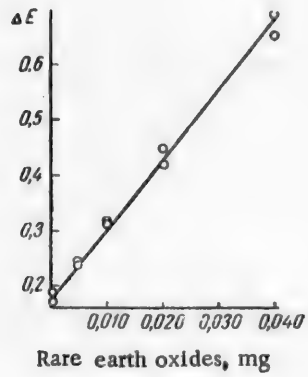


Fig. 7. Calibration curve for the determination of total rare earths in the presence of Th. Reagent—arsenazo; λ = 576 mμ; cuvette length 40 mm.

Thermospectrophotometric Determination of Total Rare Earths in the Presence of Thorium. (Thorium concentration in terms of the oxide 0.23 mg ThO_2 in 25 ml).

Rare earths, in terms of the oxides taken: rare earth oxides in the total oxides, %	taken: γ in 25 ml	γ in 25 ml found	Relative error, %
1,16	3,0	3,6	+20,0
1,16	3,0	2,8	— 6,7
1,16	3,0	3,5	+16,7
1,16	3,0	3,4	+13,3
1,16	3,0	2,5	—16,7
	Mean	3,2	+ 6,7
1,92	5,0	5,4	+ 8,0
1,92	5,0	4,9	— 2,0
1,92	5,0	5,3	+ 6,0
1,92	5,0	5,5	+10,0
1,92	5,0	4,5	—10,0
	Mean	5,1	+ 2,0
3,77	10,0	10,3	+ 3,0
3,77	10,0	10,7	+ 7,0
3,77	10,0	9,4	— 6,0
	Mean	10,1	+ 1,0
5,56	15,0	15,4	+ 2,7
5,56	15,0	14,2	— 5,3
	Mean	14,8	— 1,3
14,89	35,0	36,2	+ 3.4
14,89	35,0	34,3	— 2,0
	Mean	35,3	+ 0,9

During the analysis of precipitated oxalates, the latter together with the filter are transferred to a 100 ml quartz beaker and 10 ml each of concentrated hydrochloric, perchloric, and nitric acid added; the beaker is covered with a cover glass and the mixture heated, first on a sand bath until the filter has decomposed, and then, after removing the cover glass, on an air bath* until white fumes cease to come off. The residue is dissolved in 10 ml of 1 N HNO_3 and the solution transferred to a 100 ml standard flask, the cover glass is rinsed with water and the volume made up to 100 ml.

In order to assess the thorium concentration, 1.00 ml of the solution thus obtained is transferred to a 25 ml flask and about 5 ml of water added, followed by 2 drops of 0.1% phenolphthalein solution, 0.1 N NaOH is added until a red color is obtained which is destroyed by addition of 0.1 N HCl. Another 2 ml of 0.1 N HCl is added, this is followed by 4.0 ml of 0.3% arsenazo solution, 2 ml of the buffer mixture with a pH of 2.0 and the volume made up to the mark with water. The solution is photometrically measured against a solution of the reagent in a 10 mm cuvette at 576 mμ; the concentration of the thorium in the solution in the 100 ml flask is finally

*An air bath constructed as follows is suitable: an asbestos grid is placed 7 cm above a 600 watt electric hot plate supplied at a voltage of 220 volts.

calculated by means of the formula:

$$C_{Th} = E/3{,}70 \text{ mg/ml } ThO_2$$

(E is the light absorption of the solution).

The coefficient 3.7 corresponds to the light absorption given by 1.00 mg ThO_2 in 25 ml.

In order to determine the concentration of the rare earths, an aliquot of the test solution is taken which contains 0.23 mg of ThO_2, and the procedure outlined for the construction of a calibration curve then followed. Three to five determinations are carried out and the mean value taken.

SUMMARY

Thermospectrophotometry is the term given to the technique in which light absorption is determined at two different temperatures.

The reagent arsenazo forms soluble complex compounds with thorium and with the rare earths, and the violet colors of solutions of these complexes behave differently at different pH on heating. On changing the temperature of a solution with a pH of 3.7 from 20 to 80°, the optical density at 576 mμ of the thorium complex does not change, while that of the complex of the rare earths increases by 1.9 (La) to 2.9 (Yb) times. By using a calibration curve and carrying out photometric determinations at 20 and 80°, it is possible to determine the content of rare earths in thorium preparations, starting at a concentration of 1.2% of the rare earths in terms of their oxides. For 1.2% of the rare earth oxides in ThO_2 the experimental error is 7%, while for 15% of the rare earth oxides the error is 1%.

The apparatus and analytical procedure used are described.

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INVESTIGATION OF COMPLEX FORMATION IN SOLUTION BY THE PARTITION METHOD. THE SYSTEM SELENOYL-2-ACETONE-Th (IV)–$CHCl_3$–H_2O

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The partition method (or extraction method) which has been successfully developed in recent years by a number of research workers [1-4] is being widely used for studying the physicochemical characteristics of various complex compounds. By means of this method the instability constants and partition coefficients of the complexes of many metals both with organic and inorganic addenda, have been determined [5-10, 12] in various two phase systems. The work described here is devoted to the study of complex formation of thorium with selenoyl-2-acetone using chloroform as the organic solvent. The values of the dissociation constants and the partition coefficient of selenoyl-2-acetone in the systems $CHCl_3$–H_2O and C_6H_6–H_2O, necessary for calculating the characteristics of the complex formation process, were established previously [11].

All the experiments on the study of the partition of thorium between the organic and aqueous phases were carried out at an initial concentration of thorium in the aqueous phase of 1.0×10^{-6} g. ion/liter, a temperature of 25 ± 0.1° and an ionic strength of 0.1. The radioactive isotope Th^{234}, which was isolated from uranyl nitrate by ether extraction, was used for the work. Selenoyl-2-acetone was synthesized and purified as described earlier [11]; the preparation obtained was kept in a desiccator until its weight was constant. In order to prepare solutions of the reagent, aliquots of the latter were dissolved in a known volume of chloroform or benzene. The organic solvents were carefully purified and their purity controlled by determining their refractive indices ($n_D^{20} = 1.5013$ for C_6H_6 and $n_D^{20} = 1.4468$ for $CHCl_3$). In its remaining details the method did not differ from that described earlier [12]. It was established beforehand that in the absence of selenoyl-2-acetone in the $CHCl_3$ layer, thorium is not extracted from the aqueous phase. A series of experiments were carried out at an original concentration of thorium in the aqueous phase of 9.0×10^{-6} g. ion/liter. The near agreement of the values for the partition coefficients, obtained at concentrations of 1.0×10^{-6} and 9.0×10^{-6} g. ion/liter in the original aqueous solution, testifies to the absence of multinuclear complexes, hydrolysis products, and other polymerized particles, within the concentration range of Th^{4+} chosen [2]. The results of our experiments are in complete agreement with those described earlier for the system 2-hydroxy-1, 4-naphthoquinone–Th^{4+}–$CHCl_3$–H_2O [12].

In order to establish the composition of the complexes formed in the aqueous phase, partition curves* were taken for thorium selenoyl-2-acetonate at three successively decreasing concentrations of the reagent in the $CHCl_3$ layer. It is known [2] that the partition curves for the metal between the phases $\log q = f(pH)$ and $\log q = f(\log [HA][H^+]^{-1})$ have a different but completely definite shape in accordance with the type of complex formed. The values obtained for the partition coefficients of thorium at concentrations of selenoyl-2-acetone in the $CHCl_3$ layer of 4×10^{-2} M, 1.0×10^{-1}, and 4.0×10^{-1} M are shown in Table 1. The curves relating log q to pH and $\log [HA][H^+]^{-1}$ (Figs. 1 and 2 respectively) are in complete agreement with theoretical considerations for complexes of the type $MA_n^{(N-n)+}$ (N is the charge on the metal ion). In order to establish the possibility of the

*Henceforth the following designations are used: HA for the molecule of the organic reagent; A for the addendum; pA the reciprocal logarithm of the concentration of free addenda and $q = \Sigma[M]_{organic}/\Sigma[M]_{aqueous}$ is the partition coefficient of the metal.

TABLE 1

Partition of Th^{4+} in the System $CHCl_3-H_2O$ for Various Concentrations of the Reagent in the $CHCl_3$ layer (t = 25± 0.1°, μ = 0.1)

$[HA]^{\bullet}_{org.} = 4{,}0\cdot10^{-2}$ M				$[HA]^{\bullet}_{org.} = 1{,}0\cdot10^{-1}$ M				$[HA]^{\bullet}_{org.} = 4{,}0\cdot10^{-1}$ M			
pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q	pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q	pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q
2,40	2235	30	—1,87	2,30	2430	60	—1,61	2,40	795	1582	+0,30
2,70	1200	45	—1,43	2,40	1710	75	—1,36	2,62	219	2271	+1,01
3,50	120	465	+0,59	2,80	930	450	—0,32	2,70	195	2340	+1,08
3,60	120	622	+0,72	3,00	285	465	+0,21	2,90	132	2536	+1,28
3,70	75	870	+1,06	3,30	135	1200	+0,95	3,00	102	2667	+1,42
3,90	45	1230	+1,44	3,40	90	1305	+1,08	3,12	30	2689	+1,95
4,00	14	1200	21,90	3,50	105	1350	+1,09	3,25	21	2641	+2.10
				3,65	60	1665	+1,44	3,55	7	2814	+2,60

TABLE 2

Partition of Thorium in the Systems $CHCl_3-H_2O$ and $C_6H_6-H_2O$

$CHCl_3-H_2O$				$C_6H_6-H_2O$			
pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q	pH	I_{H_2O} imp/min	I_{CHCl_3} imp/min	log q
2,40	2235	30	—1,87	2,40	1500	24	—1,80
2,70	1200	45	—1,43	2,75	851	135	—0,80
3,50	120	465	+0,59	2,80	841	172	—0,68
3,60	120	622	+0,72	3,05	366	292	—0,10
3,70	75	870	+1,06	3,10	331	252	—0,11
3,90	45	1230	+1,44	3,36	78	544	+0,84
4,00	15	1200	+1,90	3,40	75	570	+0,88
				3,70	30	900	+1,48

formation of complexes containing molecules of the organic solvents used, curves were obtained relating the partition coefficient of selenoyl-2-acetone to the pH in the systems $CHCl_3-H_2O$, and $C_6H_6-H_2O$ for an equal concentration of the reagent in the aqueous phase. It has been established [2] that in those complexes into whose composition molecules of chloroform or benzene or another organic solvent do not enter, the curves log q = f (pH) for the condition indicated above $[HA]_{aq.}$ = const, are almost parallel. The vertical distances between curves of this type, which are numerically equal to the ratio of the corresponding partition coefficients, are almost constant throughout the whole pH range studied. The values obtained for the partition coefficients of thorium at various pH's for the system $CHCl_3-H_2O$ and $C_6H_6-H_2O$ are given in Table 2 and in Fig. 3.

The nature of the curves obtained corresponds to the case of complexes which do not contain molecules of benzene or chloroform. Thus, it can be regarded as established that under the conditions chosen, only uninuclear complexes $ThAn_n^{(4-n)+}$, which do not contain molecules of chloroform or benzene, are formed. The general relation between the partition coefficient q and the concentration of free addendum, according to Rydberg [1, 2], is established by the equation :

$$q = -\frac{\lambda_4' \cdot \varkappa_4 [A]^4}{\sum_{n=0}^{n=N} \varkappa_n [A]^n}, \qquad (1)$$

where λ_4' is the partition coefficient of ThA_4, $\varkappa_n$ is the general constant of complexity, N is the maximum number of addenda which can combine with the Th^{4+} ions. The concentration of the free addendum is calculated by

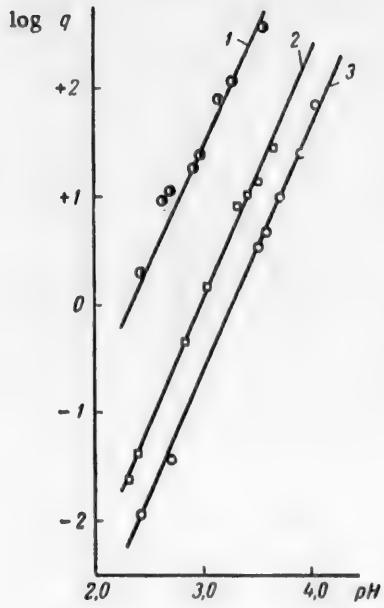

Fig. 1. Partition of Th^{4+} in the system $CHCl_3-H_2O$ as a function of the pH at various concentrations of selenoyl-2-acetone: 1) $[HA]^{o}_{org.} = 4.0 \times 10^{-1}$ M; 2) $[HA]^{o}_{org.} = 1.0 \times 10^{-1}$ M; 3) $[HA]^{o}_{org.} = 4.0 \times 10^{-2}$ M.

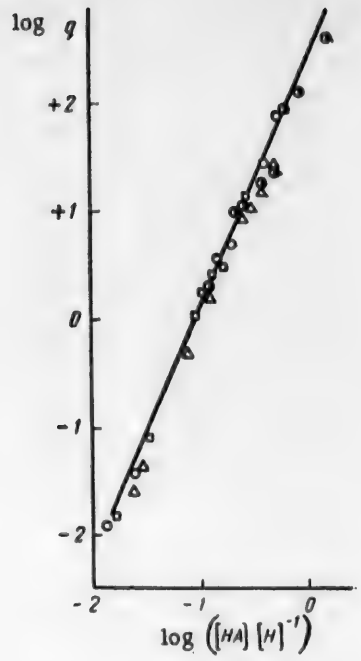

Fig. 2. Partition of Th^{4+} in the system $CHCl_3-H_2O$ as a function of log $[HA]\,[H^+]^{-1}$ at various concentrations of selenoyl-2-acetone: ○) $[HA]^{o}_{org.} = 4.0 \times 10^{-2}$ M; □) $[HA]^{o}_{org.} = 6.6 \times 10^{-2}$ M; △) $[HA]^{o}_{org.} = 1.0 \times 10^{-1}$ M; ●) $[HA]^{o}_{org.} = 4.0 \times 10^{-1}$ M.

by means of formula (2):

$$-\log[A] = pA = pK_{dis.} + \log[H^+] - \log[HA] \log + \\ + \lg(K_{par.} + 1 + K_{dis.}[H^+]^{-1}), \qquad (2)$$

where $K_{dissoc.}$ is the dissociation constant of selenoyl1-2-acetone, $K_{partit.}$ is the partition coefficient of the latter in the system $CHCl_3-H_2O$, $[HA]_{total}$ is the concentration of the reagent in the original solution, $[H^+]$ is the hydrogen ion concentration in the aqueous phase; $pK_{dissoc.} = -\log K_{dissoc.}$. The values of $K_{dissoc.}$ and $K_{partit.}$ were determined earlier [11] and are equal to respectively: $K_{dissoc.} = 2.82 \times 10^{-9}$ and $K_{partit.} = 839 \pm 9$. By introducing into equation (1) the auxiliary constant φ_n

$$\varphi_{4-n} = \frac{[ThA_n][A]^{4-n}}{[ThA_4]} = \varkappa_n \varkappa_4^{-1}, \qquad (3)$$

equation (1) can be represented in the form of a function F_n which enables one to calculate φ_n, and then the general $\varkappa_n$, and the successive k_n complexity constants by means of techniques similar to the method of Leden [13]:

$$F_0 = \frac{1}{q} = (1 + \varphi_1[A]^{-1} + \varphi_2[A]^{-2} + \varphi_3[A]^{-3} + \varphi_4[A]^{-4}) \cdot \lambda_4'^{-1}; \qquad (4)$$

$$F_1 = \left(\frac{\lambda_4'}{q} - 1\right)[A] = \varphi_1 + \varphi_2[A]^{-1} + \varphi_3[A]^{-2} + \varphi_4[A]^{-3}: \qquad (5)$$

TABLE 3

Relation between Log q and Concentration of Selenoyl-2-acetone in the Aqueous Phase

pH	$[HA]^{\bullet}_{CHCl_3}$ M	pA	log q	pH	$[HA]^{\bullet}_{CHCl_3}$ M	pA	log q
2,32	$6,6\cdot10^{-2}$	10,33	−1,84	3,12	$4,0\cdot10^{-1}$	8,75	+1,95
2,30	$1,0\cdot10^{-1}$	10,17	−1,61	3,20	$6,6\cdot10^{-2}$	9,45	+0,45
2,40	$4,0\cdot10^{-2}$	10,47	−1,87	3,25	$4,0\cdot10^{-1}$	8,62	+2,10
2,40	$4,0\cdot10^{-1}$	9,47	+0,30	3,30	$6,6\cdot10^{-2}$	9,35	+0,49
2,40	$1,0\cdot10^{-1}$	10,07	−1,36	3,30	$1,0\cdot10^{-1}$	9,17	+0,95
2,62	$4,0\cdot10^{-1}$	9,25	+1,01	3,40	$1,0\cdot10^{-1}$	9,07	+1,09
2,62	$6,6\cdot10^{-2}$	10,03	−1,10	3,50	$4,0\cdot10^{-2}$	9,37	+0,59
2,70	$4,0\cdot10^{-2}$	10,17	−1,43	3,50	$6,6\cdot10^{-2}$	9,15	+1,08
2,70	$4,0\cdot10^{-1}$	9,17	+1,08	3,50	$1,0\cdot10^{-1}$	8,97	+1,18
2,80	$1,0\cdot10^{-1}$	9,67	−0,32	3,55	$4,0\cdot10^{-1}$	8,32	+2,60
2,90	$4,0\cdot10^{-1}$	8,97	+1,28	3,60	$4,0\cdot10^{-2}$	9,27	+0,72
3,00	$1,0\cdot10^{-1}$	9,47	+0,21	3,65	$1,0\cdot10^{-1}$	8,82	+1,44
3,00	$4,0\cdot10^{-1}$	8,87	+1,42	3,70	$4,0\cdot10^{-2}$	9,17	+1,06
3,05	$6,6\cdot10^{-2}$	9,60	+0,05	3,90	$4,0\cdot10^{-2}$	8,97	+1,44
3,10	$6,6\cdot10^{-2}$	9,55	+0,26	4,00	$4,0\cdot10^{-2}$	8,87	+1,90

TABLE 4

Basic Characteristics of Complex Formation Processes in the System Selenoyl-2-acetone Th(IV) – $CHCl_3-H_2O$ (t = 25° ± 0.1°, μ = 0.1)

Partition coefficient of ThA_4	Auxiliary constants φ_n	Successive complexity constants	General complexity constants
$\lambda'_4=556\pm21$	$\varphi_1=1,4\pm0,1\cdot10^{-9}$ $\varphi_2=1,7\pm0,1\cdot10^{-18}$ $\varphi_3=1,7\pm0,1\cdot10^{-27}$ $\varphi_4=1,5\pm0,1\cdot10^{-37}$	$\kappa_1=1,1\pm0,1\cdot10^{10}$ $\kappa_2=1,0\pm0,1\cdot10^{9}$ $\kappa_3=8,0\pm0,6\cdot10^{8}$ $\kappa_4=7,1\pm0,5\cdot10^{8}$	$\varkappa_1=1,1\cdot10^{10}$ $\varkappa_2=1,1\cdot10^{19}$ $\varkappa_3=8,8\cdot10^{27}$ $\varkappa_4=6,6\cdot10^{36}$

$$F_3=\left(\frac{\lambda'_4}{q}-1\right)[A]^4=\varphi_4+\varphi_3[A]+\varphi_2[A]^2+\varphi_1[A]^3. \qquad (6)$$

The experimental values we obtained for log q at various values of pA are given in Table 3; the corresponding partition curve used for successive calculations of function F_n is shown in Fig. 4.

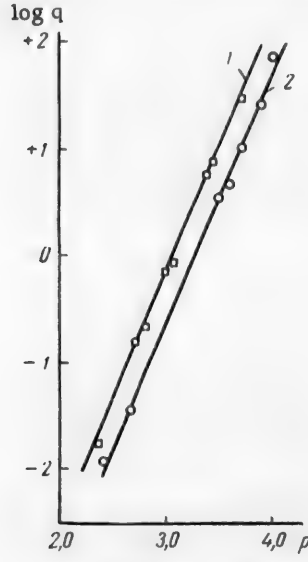

Fig. 3. Partition of thorium in the systems $C_6H_6-H_2O$ (1) and $CHCl_3-H_2O$ (2).

The curve for the function F_0 is shown in Fig. 5. Curves for successive F_n functions are not given, since they are similar in nature to F_0, while their values are readily calculated by means of equations (5-6). The method of deriving the auxiliary constants is exactly similar to that described previously [12]. The values which we found for the constant φ_n, and the successive and general constants of complexity, and also the partition coefficients of thorium selenoyl-2-acetonate in the system $CHCl_3-H_2O$ are given in Table 4.

The values obtained for the characteristics of the process of complex formation in the system examined were used for calculating the percentage distribution of thorium between complexes of various composition as a function of the same value. The corresponding curves are shown in Fig. 6a and 6b.

Thorium selenoyl-2-acetonate, in its physicochemical characteristics essentially differs from the complex compounds of Th^{4+} with other reagents containing groups with identical reactivity. A comparison of the complexity constants obtained for thorium selenoyl-2-acetonate with those determined

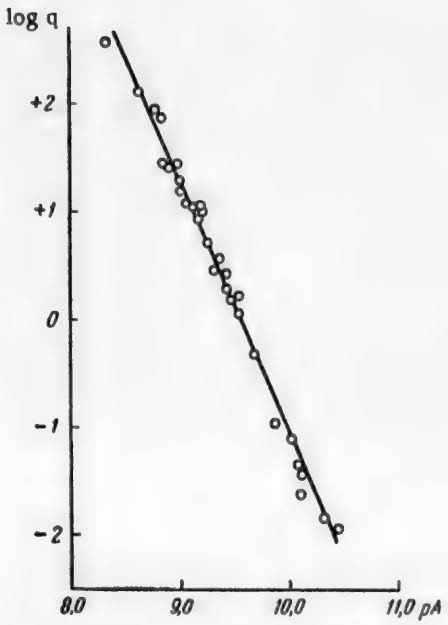

Fig. 4. Partition curve for Th^{4+} in the system $CHCl_3-H_2O$.

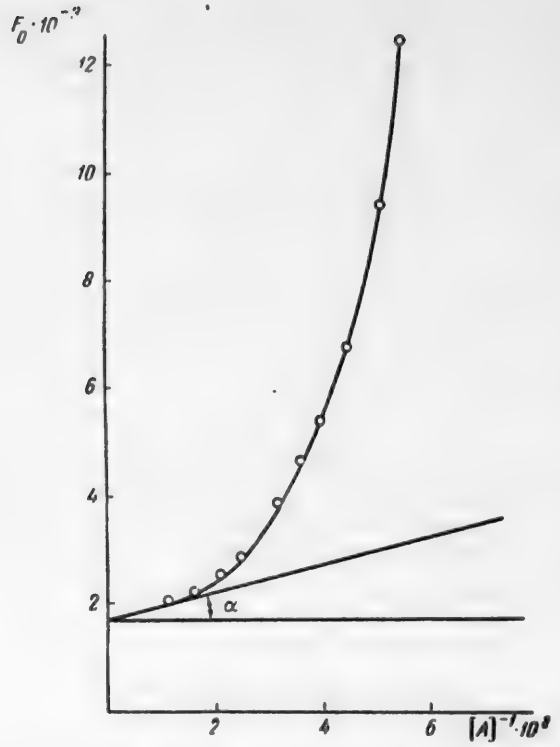

Fig. 5. Curve for function F_0.

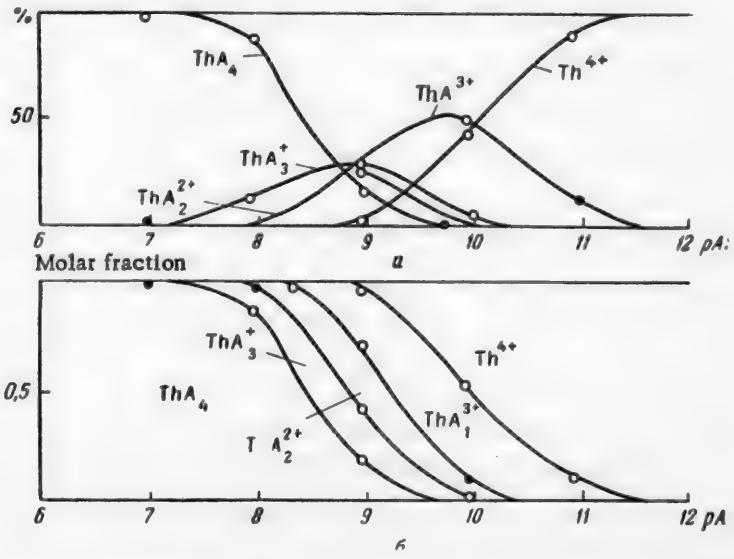

Fig. 6. Percentage distribution of thorium between complexes of differing composition (a), and the molar fraction of the various complexes (b) as a function of the concentration of the free addendum.

earlier for the acetylacetonate [14] and 2-hydroxy-1, 4-naphthoquinonate complexes [12], indicate that the former have a considerably higher stability (the general complexity constants κ_4 are respectively equal to $6.6 \cdot 10^{36}$, $1.0 \cdot 10^{27}$ and $1.5 \cdot 10^{16}$). The partition coefficient of thorium selenoyl-2-acetonate in the system $CHCl_3-H_2O$ ($\lambda_4^1 = 556$) is considerably higher than the partition coefficient, in the same system, of both the

2-hydroxy-1, 4-naphthoquinonate (λ_4^1 = 13.6), and acetylacetonate (λ_4^1 = 350 ± 20) of thorium [15]. The partition coefficient of thorium selenoyl-2-acetonate in the system $CHCl_3-H_2O$ (Fig. 3) and is somewhat higher than the corresponding characteristic of thorium acetylacetonate (for the latter λ_4^1 in C_6H_6 = 320 [14]). A similar state of affairs was observed for the partition coefficients of the reagent itself in the same systems $K_{partit.\ CHCl_3-H_2O}$ = 839 ± 9; $K_{partit.\ C_6H_6-H_2O}$ = 1009 ± 23 [11].

The partition coefficient of thorium selenoyl-2-acetonate under identical pH values depends to a considerable extent on the reagent concentration in the layer of organic solvent, which is, of course, determined by the different concentration of addendum in the aqueous phase. As is evident from Fig. 1 the partition coefficients of thorium in the system $CHCl_3-H_2O$ at pH 3, and at reagent concentrations in the $CHCl_3$ layer of 4.0×10^{-2} M, 1.0×10^{-1} M, and 4.0×10^{-1} M, are respectively equal to $q_1 = 0.22$, $q_2 = 1.12$, and $q_3 = 31.62$. In other words the percentage extraction of thorium in the layer of organic solvent $E = 100\ q/1 + q$ differs according to the concentration of the reagent at the same pH value (for the reagent concentrations indicated above, and at a pH of 3, the percentage extraction of thorium is given by $E_1 = 17.2$, $E_2 = 52.8$, $E_3 = 94.7$). 99% extraction of thorium for these concentrations of selenoyl-2-acetone is obtained respectively at pH 3.20, pH 3.85, and pH 4.15 (Fig. 1).

In the system examined it was established that only mononuclear complexes of the type $ThA^{(4-n)+}$, not containing molecules of the organic solvent in their composition, are formed. This is similar to the position observed in other systems studied earlier [1, 2, 12, 14]. The high values for the partition coefficients made it possible to take partition curves in the pH range up to 4, which decreased the probability of the formation of multinuclear complexes.

SUMMARY

As a reagent for extracting thorium from aqueous solutions, selenoyl-2-acetone is much more suitable than acetylacetone which is widely used for this purpose. The stability constants of thorium selenoyl-2-acetonate, and the partition coefficient of the complex being extracted in the system $CHCl_3-H_2O$, are considerably higher than the corresponding characteristics of the acetylacetonate complexes of the element indicated.

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THE EFFECT OF ORGANIC SOLVENTS ON THE CHROMATOGRAPHIC SEPARATION OF Li^+, Na^+, AND K^+ IONS ON SULFORESINS

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The chromatographic separation of the alkali elements in aqueous solutions has been dealt with in a number of papers by foreign workers. A fairly complete review of the literature on this question has been given in the article by Shchipakina, Nemirovskaya, and Senyavin [1]. The authors of this article were unable to achieve quantitative separation of sodium and potassium on the sulforesins SBS, SDV-1, and KU-2.

Most of the work carried out hitherto has been devoted to the separation of sodium and potassium on the sulforesins IR-100, Dowex-50. Jentzsch and Frotscher [2] obtained the best results, but their method requires 24 hours to separate a mixture containing 6 mg·equivalents each of LiCl, NaCl, and KCl on a meter long column of Wofatite KPS.

It has been shown in a series of papers [3-7] that the nature of the solvent in which the ion exchange reaction takes place has a considerable effect on the value of the exchange equilibrium constant.

During a systematic study of the effect of methanol and acetone on the exchange equilibrium of the ions Li^+, Na^+, and K^+ on the H-form of various sulforesins, we showed [8, 9] that with increasing concentration of the organic solvent, the difference in the values of the equilibrium constants increases. This led us to the idea of using mixed aqueous-organic solvents for improving the chromatographic separation of the ions.

Only two papers have been published on the separation of the alkaline elements in aqueous-organic solutions, these are: the paper by Okuno, Honda, and Ishimoru [10] who obtained fair results during the separation of Li^+, Na^+, and K^+ on amberlite-120 in 20-30% methanol; while the other paper is that by Davies and Owen [11]; using a meter long column of Zeokarb-225 they obtained good separation of a mixture containing 1 mg·equivalent each of LiCl, NaCl, and KCl, on eluting the column with a 0.7 N solution of HCl in 80% acetone. Nevertheless, one separation by their method takes about 100 hours.

The aims of the work described here were: to study the chromatographic separation of the alkali elements on sulforesins, to establish the effect of the addition of organic solvents on the separation, and to choose the optimum conditions for separating sodium and potassium, and mixtures of lithium, sodium, and potassium. Of the greatest interest was separation in mixed solvents, in that concentration range of the organic solvent (60-80%), within which the equilibrium constants of the exchange of the separated ions for hydrogen differ most.

The work was carried out on industrial samples of the cation exchange resins Espatite-1, KU-2, and SDV-3. The particle diameter was 0.25-0.5 mm for the first two resins, and 0.10-0.25 mm for SDV-3. Columns 15 mm in diameter but of varying lengths were used.

Before commencing an experiment, the column containing the resin in the H-form was washed with the solvent which was to be used for the work. A mixture of 1 N solutions of the chlorides of the cations to be separated was then introduced into the top of the column. The acid liberated was washed out with the appropriate solvent (this is essential when the analysis is based on change in acid concentration), after which the cations were eluted with a solution of HCl in this solvent. The eluates issuing from the column were then collected in separate

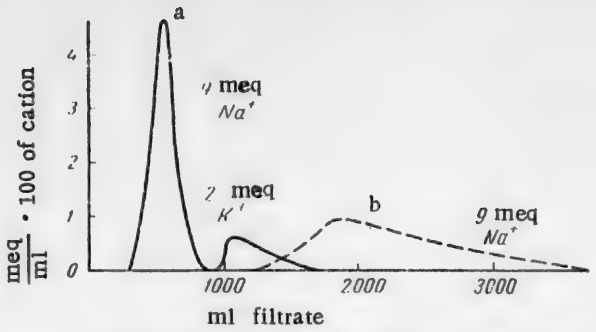

Fig. 1. Separation of sodium and potassium on Espatite; by eluting with 0.1 N HCl. a) Solvent—water, rate at which acid is passed through—3.9 ml/minute; b) solvent—60% acetone, rate at which acid is passed through—5.3 ml/minute.

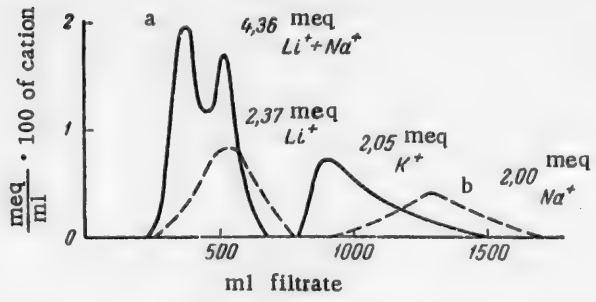

Fig. 2. Separation of lithium, sodium, and potassium on Espatite by eluting with 0.1 N HCl. a) Solvent—water, rate at which acid is passed through—0.7 ml/minute; b) solvent—60% methanol, rate at which acid is passed through—0.7 ml/minute.

fractions of 10-70 ml each. The elution was controlled by means of a spectroscope and by means of the color of a flame. The amount of the metal ions was determined either by the change in the concentration of the acid issuing from the column, or by evaporating the fractions to dryness and titrating the chloride with silver nitrate, using fluorescein as an indicator. Both methods gave results in agreement with each other.

Separation of Na^+ and K^+ on Espatite. A mixture of NaCl and KCl containing 11 mg·equivalents was poured into a column containing 36 g of Espatite. Preliminary tests showed that in order to separate the zones during elution of the cations with 0.1 N aqueous HCl, the optimum rate for passing through the acid was of the order of 5-6 ml/minute. Eluting at a higher rate does not lead to separation. Dropping the rate from 5.4 to 1.2 ml/minute improves the separation and decreases zone merging somewhat, but separation takes much longer.

In Fig. 1 are shown the results of experiments on separating 9 mg·equivalents of sodium and 2 mg·equivalents of potassium in water and 60% acetone. In an aqueous acetone solution it was possible to achieve quantitative separation of sodium from potassium, since Na^+ was eluted with 0.1 N HCl in 60% acetone solution, while K^+ was not detected even after 1000 ml of eluate had been collected. Similar results were obtained for other ratios of sodium to potassium.

Separation of Mixtures of Li^+, Na^+, and K^+ on Espatite. Into a column of the same dimensions as that used in the previous tests was poured a mixture consisting of 2.39 mg·equivalents of LiCl and 2 mg·equivalents each of NaCl and KCl. The column was washed either with an aqueous or an aqueous alcohol solution of HCl. Some of the results are given in Fig. 2. It was found that in water the lithium and sodium zones overlap considerably. The use of a 60% methanol solution made it possible to separate the given mixture quantitatively, the intermediate eluate between lithium and sodium was greater than 100 ml, potassium was not eluted with 0.1 N aqueous alcoholic hydrochloric acid. Increasing the rate at which acid was poured through the column from 0.7 to 2.2

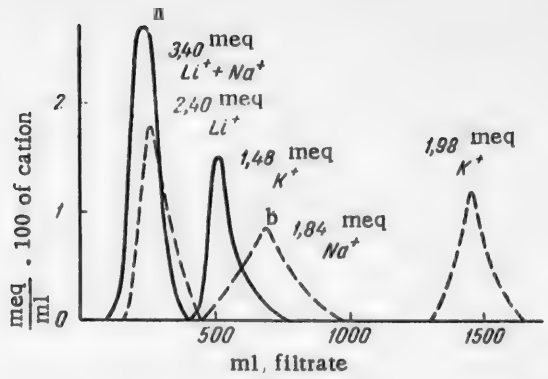

Fig. 3. Separation of lithium, sodium, and potassium on Espatite by eluting with 0.28 N HCl. a) 1.9 mg·equivalents LiCl, 1.5 mg·equivalents NaCl, and 1.5 mg·equivalents KCl; solvent—water; rate at which acid passes through —1.2 ml/minute; b) 2.4 mg·equivalents LiCl, 1.9 mg·equivalents NaCl, and 2.0 mg·equivalents KCl; solvent—60% methanol, rate at which acid is passed through—1.3 ml/minute.

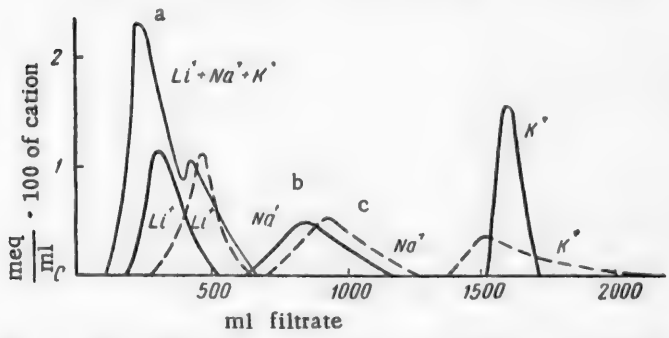

Fig. 4. Separation of a mixture of 1.8 mg·equivalents of LiCl, 1.5 mg·equivalents NaCl, and 1.5 mg·equivalents KCl on SDV-3 by eluting with 0.1 N HCl. a) Solvent—water; rate at which acid is passed through—1.5 ml/minute, b) solvent—60% methanol, rate at which acid is passed through 2.5 ml/minute; c) solvent—60% acetone, rate at which acid is passed through—1.4 ml/minute.

ml/minute did not lead to a deterioration of the separation. In this case, however, the zones were somewhat more diffuse, but the volume of intermediate eluate between Li^+ and Na^+ did not change. In order to reduce the time required it is more convenient to accelerate elution.

In the experiment described, separation demanded a fairly long time. Accordingly, in our subsequent experiments we used a more concentrated acid for eluting (Fig. 3).

On using 0.28 N hydrochloric acid in 60% methanol (Fig. 3b) the zones of lithium and sodium hardly overlapped at all, and, after eluting the sodium, potassium was absent in at least the next 300 ml of eluate (K^+ was eluted here, as in similar cases, with 0.3 N aqueous HCl). In aqueous media, on using 0.28 N HCl, even when smaller amounts of the cations were used (Fig. 3a) Li^+ and Na^+ were eluted together and the interval between Na^+ and K^+ dropped to only 15 ml. Thus, by using Espatite, it is fairly easy to separate, in many cases, sodium and potassium, while by means of a 0.1 N solution of HCl in 60% methanol it is possible to carry out a quantitative separation of lithium, sodium, and potassium.

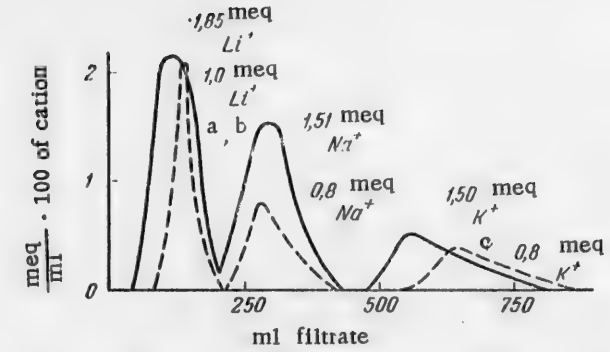

Fig. 5. Separation of lithium, sodium, and potassium on SDV-3 by eluting with 0.28 N HCl in 60% methanol. a) 1.9 mg·equivalents LiCl, 1.5 mg·equivalents NaCl, and 1.5 mg·equivalents KCl, rate at which acid is passed through—0.8 ml/minute; b) 1.9 mg·equivalents LiCl, 1.5 mg·equivalents NaCl, and 1.5 mg·equivalents KCl, rate at which acid is passed through -2.4 ml/minute; c) 1.0 mg·equivalents LiCl, 0.8 mg·equivalents NaCl, and 0.8 mg·equivalents KCl, rate at which acid is passed through —1.4 ml/minute.

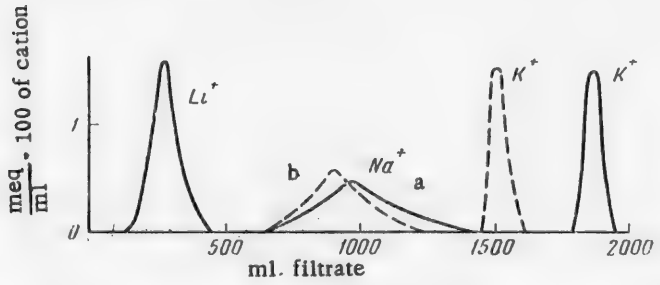

Fig. 6. Separation of a mixture of 1.9 mg·equivalents LiCl, 1.5 mg·equivalents NaCl, and 1.5 mg·equivalents KCl on SDV-3 in 80% methanol. a) Elution with 0.12 N HCl at the rate of 3.5 ml/minute; b) elution rate—5.4 ml/minute. Initial HCl concentration—0.12 N; after 660 ml of eluate had been collected 0.24 N HCl was used, while after 1450 ml of eluate, 0.6 N HCl was used.

Separation of Na^+ and K^+ on KU-2. The exchange equilibrium constants for the ions to be separated on the H-form of the cation exchange resin KU-2 are respectively 1.49 and 2.34 for water, and 8.42 and 16.70 for 60% methanol (the method used for determining these values has been described earlier [3]). Accordingly, one should expect here again that there will be an improvement in the separation on using 60% methanol.

During the separation of a mixture of 3 mg·equivalents NaCl and 1 or 2 mg·equivalents of KCl on a column 20 cm long and containing 12 g resin, and using 0.1 N aqueous HCl, the sodium and potassium zones did not overlap, although the interval between them was not very large. The use of 60% methanol as the solvent permitted, as in the case of Espatite, ready separation of Na^+ from K^+.

Separation of Li^+, Na^+, and K^+ on SDV-3. The work was carried out on a column 17 cm long and containing 10 g of resin. In Fig. 4 are shown the results obtained on using 0.1 N HCl. In water (Fig. 4a) the zones of all three cations overlapped. In 60% methanol (Fig. 4b) a good quantitative separation of all the ions was effected. Again in this case, as was the case with Espatite and KU-2, potassium was not eluted with 0.1 N HCl.

On carrying out a separation in a medium of 60% acetone (Fig. 4 c) satisfactory results were obtained. The interval between Li^+ and Na^+ in the eluate was about 50 ml, while that between Na^+ and K^+ was about 100 ml. In this case, K^+, just like the other cations, was eluted with 0.13 N HCl aqueous acetone.

Attempts to accelerate separation by using 0.28 N acid were less successful (Fig. 5). Naturally, in water, all the zones overlapped. In 60% methanol the Na^+ and Li^+ zones overlapped to an insignificant extent, potassium was separated satisfactorily.

Complete separation was achieved on using 80% methanol as solvent (Fig. 6). On eluting with 0.12 N HCl, the interval between lithium and sodium was about 120 ml. In order to cut down on the time, it was found expedient after eluting the lithium with 0.1 N acid, to elute sodium with 0.2 N HCl in 80% methanol, while potassium was then eluted by using a still more concentrated aqueous solution of HCl. We used 0.12 N and 0.24 N solutions of HCl in 80% methanol, and 0.6 N aqueous HCl (Fig. 6 b). The elution rate was 5.4 ml/minute.

Accordingly, it is not possible to separate mixtures of Li^+, Na^+, and K^+ on SDV-3 in aqueous solutions. The use of aqueous organic solvents gives rise to conditions under which rapid quantitative separation of these ions becomes possible.

SUMMARY

Quantitative separation of sodium and potassium in an aqueous medium is possible on Espatite and KU-2.

In aqueous media it is not possible to separate lithium from sodium, either on Espatite or on SDV-3.

On carrying out separations on sulforesins in a medium of mixed solvents, there is a considerable improvement in separation of mixtures of lithium, sodium, and potassium.

From a practical point of view, the most suitable method is chromatographic separation on SDV-3 resin, using 0.12 N and 0.25 N solutions of HCl in 80% methanol for eluting lithium and sodium respectively, and then using a more concentrated aqueous solution of HCl for eluting the potassium.

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DETERMINATION OF SMALL AMOUNTS OF COPPER IN METALS BY MEANS OF TETRAETHYLTHIURAMDISULFIDE (DICUPRAL)

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Tetraethylthiuramidisulfide $(C_2H_5)_2NC(S) \cdot S \cdot S \cdot (S)CN\,(C_2H_5)_2$ has been used for the detection [1] and photometric determination of copper [2-4]. It is readily available since it is used as an accelerator for rubber vulcanization, and is also used in tablet form as an effective means of curing alcoholism, for the latter purpose it is marketed under the names "Refusal","Antabuse", "Stopetil", etc. From such tablets it is possible to prepare pure tetraethylthiuramdisulfide by recrystallization in hot ethanol. The pure material is sparingly soluble in water, it is more soluble in organic solvents, e.g., ethanol, it exists in the form of almost colorless crystals with a melting point of 70°. An alcoholic solution of tetraethylthiuramdisulfide reacts with cupric salts Cu^{2+} in weakly acid solutions to form an intensely yellow-brown colored compound; all the other elements studied do not give such colored compounds. We propose to call tetraethylthiuramdisulfide dicupral. Only mercurous salts and selenites interfere with the detection of copper, these being reduced to the elemental state (we have made use of this fact for the gravimetric determination of selenium).

The reaction sensitivity is as follows: on a spot plate pD = 5.70, in a micro test tube pD = 5.0, by extraction with ether pD = 7.18, and on filter paper pD = 6.48. Excess nitric acid and strong oxidizing agents interfere. The absorption maximum of solutions of the copper compound lies at 435 mμ; it is suitable for the photometric determination of copper (Fig. 1).

Dicupral is a more sensitive reagent than other reagents for copper, e.g., cupral (sodium diethyldithiocarbamate). The high selectivity of the reagent permits copper to be determined in the presence of many other elements.

Silver and mercuric ions form colorless compounds with dicupral, these compounds being more stable than the corresponding compounds of copper; accordingly, the intensity of the yellow-brown color of the copper compound with dicupral decreases and decolorization subsequently occurs on addition of Ag^{+} or Hg^{2+}. Accordingly, if a test solution contains silver or mercury, excess reagent should be added in order to detect copper. On the other hand, we have used this phenomenon for the sensitive, selective determination of silver or mercury [5]. We have obtained very good results during the determination of mercury [6] or silver [7] in mineral raw materials, particularly in ores.

The photometric determination of copper by means of dicupral has justified itself in many instances, and is being used in various laboratories. One can point out for example the determination of not more than 0.005% of Cu in carbonates [8], or in the most diverse ores [9], in special forms of phosphates [10], in technical alkalis [9], in steel [11], in the blood plasma of children suffering from chest diseases (using 0.3 ml of sample) [12], etc.

The nature and the concentration of acid in solution affect the rate at which the maximum color intensity is reached, and also affect the nature of the calibration curve. In the work described here we concentrated on the optimum conditions in various media. At the same time we studied the effect of a large excess of various metals during the photometric determination of copper, and established that in many cases it is possible to determine copper in pure metals at a level of 0.01% Cu, without preliminary separation of the copper.

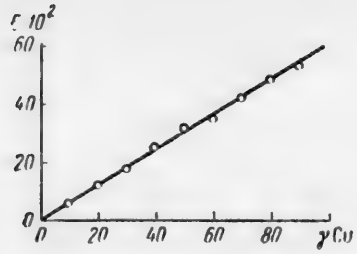

Fig. 1. Calibration curve for the determination of copper.

EXPERIMENTAL

The reagents used were as follows: a 0.01 M (0.3%) solution of tetraethylthiuramdisulfide (dicupral) in 96% ethanol. The solution of cupric sulfate (0.01 M) was prepared from the crystalline salt, the copper content was determined electrolytically. In order to maintain the hydrogen ion concentration constant, acetic (pH 4.7) and phosphoric (pH 7.0) buffer solutions were used, in addition to a dilute solution of KOH (pH 10.1); the pH was controlled by means of a glass electrode.

Twice distilled water was used for diluting the solutions. All the reagents used were checked beforehand for their copper content.

The optical density was measured on a Coleman Junior spectrophotometer type 6A with cells having a layer thickness of 16 mm, and also on a Fisher spectrophotometer AC with a blue filter 425 B, and a Pulfrich photometer.

a) Effect of the Medium. As noted already, the concentration of acid in solution affects the reaction of copper with dicupral. During a study of this reaction in media containing various acids (hydrochloric, sulfuric, nitric, and phosphoric) of differing concentrations, and also in buffered solutions (pH 4.7 and 7.0), and in weakly alkaline media, the rate at which the color intensity reached its maximum, and the stability of the color were compared. 20 μg and 50 μg of copper were taken; in both instances similar results were obtained. The procedure adopted was as follows: into a 25 ml standard flask was measured out standard solution containing exactly 20 μg or 50 μg of copper; distilled water, acid, or buffer solution was added until a definite final concentration of acid or a definite pH was reached; 6 ml of 96% alcohol was then added, followed by 3 ml of 0.01 M dicupral solution, and the solution finally made up to the mark with 96% alcohol; after mixing, the optical density was measured using a blue filter 425 B.

It is evident from the Table that with increasing acid concentration the reaction rate also increases; in strongly concentrated acid media the maximum color intensity is reached very rapidly, however, the intensity drops rapidly. In dilute acid media, and in the buffered solutions, although the reaction proceeds more slowly, the stability of the color is more than sufficient for measurement purposes.

With increasing acid concentration not only does the rate at which the color develops increase, but the color is more intense (Fig. 2).

For practical purposes it can be concluded that the calibration curves should be constructed on the basis of solutions with the same acidity as that of the test solutions. Acidity changes within small limits (1-2 N $HClO_4$, or 0.5-2N H_2SO_4, 0.5-1 N H_3PO_4, 0.1-0.5 N HCl, or 1-2 N HCl) have almost no effect on the optical density. Nitric acid at concentrations higher than 0.08 N interferes, since it reacts with the reagent. The best technique is to use a sufficient amount of the appropriate (e.g. acetic) buffer. It is necessary to carry out a careful control test for each determination, since dicupral itself acquires a weak yellow color on increasing the acidity of the solution (Fig. 3). This color is most clearly evident in hydrochloric acid solutions, since it increases directly with the concentration (even very pure hydrochloric acid usually contains traces of copper); this color does not develop in perchloric and sulfuric acids.

The presence of some organic acids (oxalic, tartaric) does not interfere with the reaction between copper and dicupral ; on the other hand, the presence of ascorbic acid, fluorides, borax, and cyanides interferes with the determination.

The absorption maximum of the colored compound of copper changes insignificantly in various media (Fig. 4).

The following useful conclusions can be drawn from the experiments we carried out: it is best to determine copper in weakly acid buffered solutions at pH 7; in more acid and strongly acid solutions the optical density should be measured within the time limits indicated in the table.

Stability of the Color of the Compound of Copper with Dicupral (20 μg Cu in 25 ml)

Medium	Time required	Time for which the color is stable
H_2SO_4, *N*		
8	10	20 min
6	10	2 hr
4	10	5 hr
2	20	5 hr *
1	20	5 hr *
0,1	30	5 hr *
0,01	30	5 hr *
HCl, *N*		
4	50	45 min*
2	15	5 hr *
1	15	5 hr *
0,1	30	5 hr *
0,01	30	5 hr *
0,001	30	5 hr *
$HClO_4$, *N*		
4	10	30 min
2	15	2 hr
1	15	2 hr
0,1	15	5 hr
0,01	15	5 hr
H_3PO_4, *N*		
6	10	5 hr
4	10	5 hr
2	10	5 hr
1	10	5 hr
HNO_3		
0,05 *N*	15	2 hr
0,08 *N*	15	1 hr
pH 4,6	15	5 hr
pH 7,0	25	5 hr
pH 0,1	20	5 hr
5% Oxalic acid solution	10	3 hr
5% Tartaric acid	20	5 hr

*Color constant after 24 hours.

b) Determination of Traces of Copper in Metals. We have already noted previously [3] the high selectivity of the determination of copper. In those cases where, at high concentrations of certain metals, high results are obtained because these metals give a very weak color similar to the color given by copper, interference on the part of such metals can be eliminated, to a significant extent, by addition of Complexon III. But in such cases all the work should be carried out in fairly acid media in which copper does not react with Complexon III.

We checked on the possibility of determining copper in synthetic mixtures containing large amounts of zinc, aluminum, mercury, tin, arsenic, antimony, tungsten, and manganese, and demonstrated that it is possible to determine copper in pure zinc and in pure aluminum without separation.

The synthetic mixtures contained 25 μg or 50 μg of copper in 25 or 50 ml of solution. The synthetic mixture was prepared as follows: to a standard flask containing the copper solution was added a solution of the salt of the appropriate metal in gradually increasing amounts until the ratio of copper to metal was 1:10,000, and, in individual cases, 1:20,000, this corresponded to a content of 0.01 to 0.005% of copper in the metal. The acidity of the solution was adjusted to the optimum value, water was added to bring the volume to half the total volume, 6 ml of 96% ethanol was added, followed by 3 ml of 0.01 M dicupral, the volume was made up to the mark with ethanol and the whole thoroughly mixed. The optical density was measured after a certain time indicated in the table for a given acidity; a control test was carried out with pure copper and with a solution of metal not containing copper. Such an order for carrying out the reactions must be accurately observed, particularly because an unsuitable ratio of water to ethanol can lead, in certain cases, to precipitation of the salt or of the reagent.

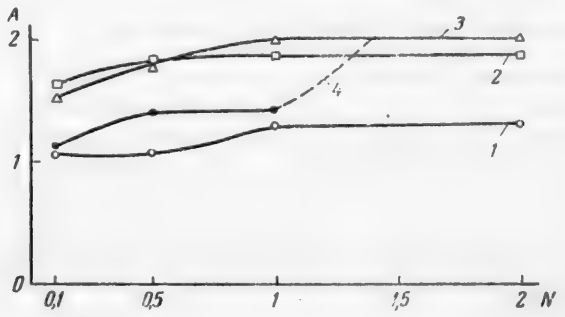

Fig. 2. Relation between the optical density of the compound of copper with dicupral and the acidity of the medium. 1) HCl, 2) H_2SO_4, 3) $HClO_4$, H_3PO_4. 40 μg Cu taken (Measurements were made after the color intensity had reached its maximum.)

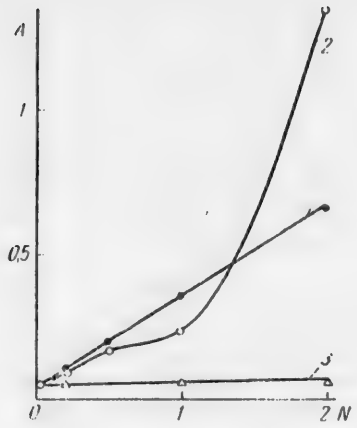

Fig. 3. Relation between optical density of dicupral and acid concentration. 1) HCl, 2) H_2SO_4, 3) H_2SO_4 and $HClO_4$.

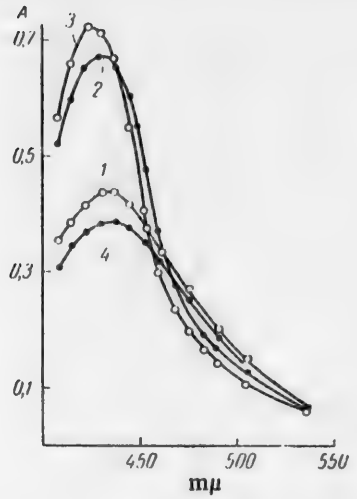

Fig. 4. Absorption of the compound of copper with dicupral in various media. 1) pH 7, 2) HCl, 3) H_3PO_4, H_2SO_4 and $HClO_4$, 4) pH 4.7.

Copper in Zinc. Measurements are carried out in a medium of 2-4 N sulfuric acid; at ratios of Cu:Zn = =1:20,000 (0.005% Cu in Zn) copper can still be determined. The optical density is measured 20 minutes after completion of the reaction.

Copper in Aluminum. Measurements are carried out in 1 N hydrochloric acid. At a ratio of 1:20,000 (0.005% Cu in Al), copper can still be determined. Optical density is measured 30 minutes after completion of the reaction. For quantities of aluminum greater than 10,000 times that of copper, it is useful to add Complexon III.

Copper in Mercury. [5] It is known that mercury ions form a more stable complex than copper with dicupral, but the complex with mercury is colorless; when large amounts of mercury are present no color develops from the copper since the reagent is used up for forming the complex with the mercury ions. Accordingly, a sufficient amount of a solution of Complexon III is added, since mercury gives an even more stable complex with Complexon than it does with dicupral. But, even in this case, copper can only be determined in mercury at a ratio of Cu:Hg of 1:2,000 (0.05% Cu in Hg). The optical density is measured in 1 N hydrogen chloride, 20 minutes after completion of the reaction.

Copper in Tungsten. For preparing synthetic samples, mixtures of solutions of cupric sulfate and sodium tungstate are used. In weakly alkaline solutions (pH 10.1) it is possible to determine copper at a ratio of Cu:W = = 1:10,000 (0.01%). Measurements are made 20 minutes after completion of the reaction.

Copper in Tin. In the presence of divalent tin salts, reduction of the reagent occurs, and the yellow color of the copper complex is decolorized; accordingly, copper can only be determined in the presence of quadrivalent tin. In a medium of 2 N hydrogen chloride, copper can be determined in the presence of tin at a ratio of Cu:Sn = = 1:500 (0.2% Cu in Sn); the optical density is measured 20 minutes after the reaction. Even traces of divalent tin (when oxidation is incomplete) in the solution decrease the color intensity.

Copper in Manganese. In 4 N sulfuric acid (the optical density being measured 15 minutes after the reaction has been carried out) copper can still be determined in the presence of manganese at a ratio of Cu:Mn = 1:6,000 without getting any high results.

Copper in Arsenic and Antimony. In 1 N hydrochloric acid, when the optical density is measured 25 minutes after carrying out the reaction, copper can be determined in the presence of arsenic at a ratio of Cu:As (Sb) = 1:1,000 (0.1% Cu in As or Sb). When higher concentrations of arsenic and antimony are present, high results are obtained.

In order to check on the practical applicability of the method, we determined copper in aluminum and zinc, using samples containing 0.01% Cu. The test zinc (5 g) was dissolved in 25 ml of concentrated sulfuric acid, while the aluminum was dissolved in 80 ml of dilute hydrochloric acid. The solution was evaporated and then cooled, the residue was dissolved in acid of the appropriate normality in a standard flask (100 ml), so that in the solution obtained the concentration of sulfuric or hydrochloric acid was 2N or N respectively. An aliquot was taken and copper then determined by the method described above.

SUMMARY

The influence of the medium, mainly the concentration and nature of the acid, on the interaction of copper salts with tetraethylthiuramdisulfide (dicupral) has been studied. The effect of a large excess of foreign cations on the photometric determination of copper has been studied and clarified. A method has been developed for the determination of small amounts of copper in pure metals.

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DETERMINATION OF SMALL AMOUNTS OF THE RARE EARTHS IN PREPARATIONS OF PRASEODYMIUM, NEODYMIUM, SAMARIUM, TERBIUM, DYSPROSIUM, HOLMIUM, ERBIUM, AND THULIUM

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Of the spectrographic methods for controlling the purity of preparations of the rare earths (r.e.), the most acceptable is analysis on the basis of their emission spectra, which permits all the rare earths to be determined without exception, and is characterized by a high, absolute sensitivity. As is evident from Table 1, Fassel and coworkers [2-4] have been mainly responsible for work on the determination of impurities in purified preparations of the rare earths on the basis of their emission spectra. According to the technique they have developed, an aliquot of 15 mg, which is a mixture of the rare earth oxides in the form of a powder, is completely burnt in a d.c. arc (17-18 amps, 220 volts) between carbon electrodes.

During the analysis of rare earth preparations using a Russian diffraction spectrograph, the DFS-3, with a dispersion of 2 A/mm in the first order, the standards and samples for quantitative determination of the impurities in the rare earths are usually prepared in the form of 5% (in terms of the metal) solutions of the rare earth chlorides in 1% HCl [10]. A drop of the solution is placed on the flat end of a copper or carbon electrode which had been covered beforehand with a film of polystyrene. After drying off the drop, there remains on the electrode face a fine layer of test material. The spectrum is excited in an a.c. arc (8 amps, 220 volts). As was shown in [10], the use of the DFS-3 spectrograph for emission analysis of purified preparations of the rare earths, despite the complexity of their spectra, made it possible to determine hundredths of a percent of the impurities which are neighbors of the rare earth series of elements. For this purpose not more than 1 mg of test material is necessary.

TABLE 1

Base	Gatterer, Jumhkes, [1]	Fassel et al. [2-4]	Shvangiradze [5, 6]	Akimov [7]	Polyakov Rusanov [8]	Brukl, Ross - manith [9]	Our results
			Impurities determined				
La	—	Ce, Pr, Nd	Ce, Pr, Nd	Ce, Pr	Ce, Pr, Nd	—	—
Ce	—	La, Pr, Nd	La, Pr	—	La	—	—
Pr	—	La, Ce, Nd	—	—	—	—	La, Nd
Nd	—	Pr, Sm	Pr, Sm	—	—	—	Pr, Sm
Sm	Eu	Eu	Eu, Nd	Nd	—	Eu, Nd	Eu, Nd
Eu	—	—	—	—	—	Sm	—
Gd	—	—	—	—	—	—	—
Tb	—	—	—	—	—	—	Gd, Y
Dy	—	Y, Tb, Ho, Er	—	—	—	—	Y, Ho
Ho	—	Y, Dy, Er	—	—	—	—	Dy, Er
Er	—	Y, Dy, Ho, Tu, Yb	—	—	—	—	Ho, Tu
Tu	—	—	—	—	—	—	Er, Yb

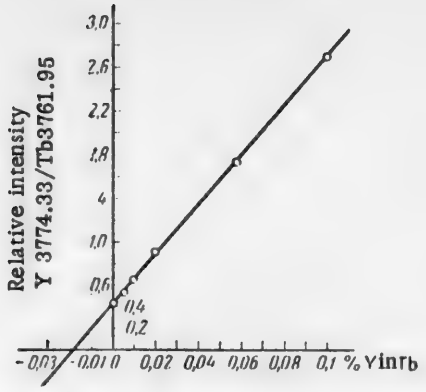

Fig. 1. Relation between the relative intensity Y 3774.33 / Tb3761.95 and the yttrium concentration of the standards.

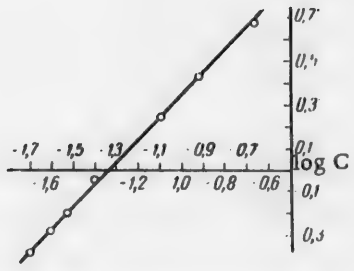

Fig. 2. Calibration curve for the determination of yttrium in terbium by means of the lines Y 3774.33 / Tb 3761.95.

In the work described here small amounts of the impurities shown in Table 1 were determined in purified preparations of terbium, dysprosium, thulium, and samarium by the technique described previously [10]. In addition, the method for the determination of impurities in erbium, holmium, and praseodymium was made more accurate.

In view of the lack of information, for our purposes, regarding the emission spectra of the rare earths, the choice of the most sensitive lines of the impurities, which were free from superposition by other lines, was made as follows. The spectra of a series of preparations, obtained, for example, during the purification of terbium preparations from yttrium and gadolinium by the method of ion exchange chromatography, were studied in the region between 3000 and 4600 A. For the determination of yttrium in terbium preparations, those lines were chosen which were most intense in the spectrum of the terbium preparation strongly contamined with yttrium and not detected in the spectrum of a terbium preparation containing the highest amount of gadolinium. The reference lines chosen were those lines lying nearest to the analytical lines of the impurity, and which belong to the element forming the major component of the test sample, and for which the value log R (R is the relative intensity) exhibits the least shift on photographing the spectrum of the same standard 5-6 times on one plate, or taking two photographs on 2-4 plates.

TABLE 2

Determination of	Analytical lines	Range of concentrations determined, %	Electrodes
Y in Tb	Y 3774,33/Tb 3761,95	0,02 —0,2	Copper
Gd in Tb	Gd 3768,41/Tb 3761,95	0,02 —1	The same
Y in Dy	Y 3774,33/Dy 3777,99	0,007—0,2	" "
Dy in Ho	Dy 4211,72/Ho 4219,13	0,02 —1	" "
Ho in Er	Ho 4103,84/Er 4104,01	0,02 —1	" "
Tu in Er*	Tu 3362,61/Er 3369,22	0,005—1	Carbon
Yb in Tu**	Yb 3289,37/Tu 3291,00	0,05 —1	The same
Yb in Tu	Yb 3987,99/Tu 3926,74	0,005—0,2	Copper
Er in Tu	Er 3906,32/Tu 3912,90	0,02 —1	The same
La in Pr	La 3337,49/Pr 3340,53	0,005—0,1	Carbon
Nd in Pr	Nd 43 8,17/Pr 4356,67	0,1 —1	The same
Sm in Nd***	Sm 4433,87/Nd 4436,68	0,05 —1	" "
Pr in Nd***	Pr 4408,84/Nd 4419,62	0,1 —1	" "
Nd in Sm	Nd 4303,57/Sm 4300,16	0,02 —1	" "
Eu in Sm	Eu 3819,66/Sm 3818,35	0,005—0,2	Copper

*When the concentration of impurities is > 0.1%, 1% solutions can be used.

**For determination of Yb in Tu in the given concentration range, we used a 0.05% solution of Tu in 1% HCl.

***These pairs of lines are given in [3].

TABLE 3

Determination of:	Initial content of impurity, %	Added, %	Total	Found, %	Error, %
Y in Tb	0,02	0,02	0,04	0 042	5
	0,02	0,02	0,04	0,038	5
Gd in Tb	0,04	0,1	0,14	0,146	4,3
	0,04	0,1	0,14	0,135	3,5

Calibration curves of log R against log c (c is the concentration in % of the impurity in the standard) were constructed for the chosen analytical pairs of lines.

For preparing the standards, the most pure preparations of the rare earths obtained during separation by ion exchange chromatography were used. Sensitive lines for yttrium were detected in the spectra of the purest terbium and dysprosium preparations, while in the spectrum of a samarium preparation the last lines of europium were found. The concentration of these impurities was determined by the method of additions [11]. In Fig. 1 are given the calibration curves*, within the coordinates R, c, which illustrate the determination of the residual yttrium as an impurity in the purest sample of terbium, on the basis of which standards of Tb and Y were prepared. As is shown in Fig. 1, the yttrium content is 0.019%. After applying this correction for the yttrium content in the standards, the calibration curve of log R against log c in the concentration range 0.02 to 0.22% was linear, and was used for the determination of yttrium present as an impurity in more impure samples. (Fig. 2). 0.007% of yttrium was found in the dysprosium preparation, while the amount of europium in a samarium preparation was 0.004%.

Table 2 contains the analytical lines which we chose, the concentration ranges for which the curves used for determining the impurities were linear, and the electrodes used.

The conditions used for taking the spectra of the rare earths being determined are given in a previous article [10].

Curves during the construction of which the residual impurities were taken into account, and were based on standards whose spectra had been photographed on 2-6 plates, preserve a constant slope (about 45°) and do not exhibit any shift. The mean arithmetic error during determination of the concentration (calculated from four experimental results) amounts to about 5%.

In order to check on the correctness of the determination of the impurities by the method indicated [10], control standards were prepared. Into a preparation containing the impurity element in an amount established beforehand, was added a known amount of the same element, after which the total amount of the element was determined. Table 3 contains as examples some of the results obtained during such determinations.

The author would like to thank G. K. Eremina and L. I. Martynenko for gifts of rare earth preparations, and V. N. Tatevskii and L. V. Lipis for helping in the work.

SUMMARY

As a result of a study of the spectra of lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, terbium, yttrium, dysprosium, holmium, erbium, thulium, and ytterbium, in the region 3000 to 4600 A, analytical lines have been chosen which are suitable for determining hundredths of a percent of the rare earths listed.

*The graphical method for calculating the concentration of residual impurity in the test preparations [11] holds for the conditions $R = ac^v$, $v = 1$. As is evident from Fig. 1. this is the case for the determination of yttrium in terbium.

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THE PHOTOMETRIC DETERMINATION OF TITANIUM IN TITANIUM BORIDES BY MEANS OF ARSENAZO

E. I. Nikitina

Arsenazo, or benzene-2-arsonic acid < 1-azo-2 > 1, 8-dihydroxy-naphthalene-3, 6-disulfonic acid, is used for the photometric determination of the rare earths [1], zirconium [2], aluminum [3], and tantalum [4]. Arsenazo in aqueous, neutral and acid solutions, has a rose color: in the presence of titanium the color changes to violet at a pH of 2-3. On increasing the acidity, the color of the compound of titanium with arsenazo gradually weakens, and at a pH of 0.7-0.8, disappears completely [4]. The relation between the color of the complex of titanium with arsenazo and the pH of the solution is shown in Fig. 1.

In solution at pH 2.5-3, titanium forms a more stable colored complex compound with arsenazo: the optical density of the solution in this acidity range remains almost constant for 0.01-0.25 mg of titanium. The solution conforms to the Beer law for amounts of 0.01 to 0.25 mg of titanium (Fig. 2). The color of the titanium complex with arsenazo is readily reproducible and is fully suitable for the photometric determination of titanium. The colored, soluble compound of titanium with arsenazo is formed at room temperature immediately after addition of reagent to a weakly acid solution of a titanium salt. The color intensity does not change on heating the solution. The color of the titanium-arsenazo compound is stable for several days. The reaction of titanium with arsenazo is considerably more sensitive than the reaction with hydrogen peroxide. It permits determination of 0.05 γ of titanium in one ml. The nature of the mineral acid does not affect the colored compound of titanium with arsenazo—it develops at pH 2-3 in hydrochloric and sulfuric acid solutions.

Titanium is best determined photometrically with arsenazo on the basis of the mixed color obtained from excess reagent and the violet color of the titanium complex. The mixed color is obtained on adding 10 ml of a 0.05% solution of reagent, for titanium contents ranging from 0.01 to 0.25 mg of titanium in 100 ml of solution.

The maximum light absorption of the titanium complex at pH 2.5-3 is located at 580 mμ (Fig. 3). In this spectral region the solution of pure arsenazo has minimum light absorption.

The results given in Table 1 show the good reproducibility obtained during the determination of titanium with arsenazo. The reagent is so sensitive to titanium, and the color is so intense, that in order to measure 0.25 mg of titanium, a cell with a layer thickness of 20 mm should be used. The zero solution used consists of 10 ml of arsenazo solution and 90 ml of water.

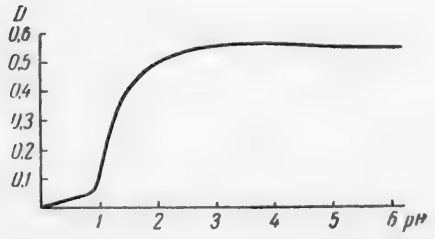

Fig. 1. The relation between the color of the titanium complex with arsenazo and the pH of the solution.

In the presence of oxalates and fluorides the compound of titanium with arsenazo is not formed (Table 2). Tartaric or citric acid in a sulfuric acid solution slightly depresses the intensity of the color of the titanium arsenazo complex (Table 2), but the sensitivity of the reaction remains unchanged (0.05 γ titanium in 1 ml).

The alkali and alkaline earth metals do not interfere with the determination of titanium by means of arsenazo. Ferric iron (up to 0.03 mg), and trivalent chromium (< 0.1 mg) present in the solution being analyzed do not interfere either with titanium determination.

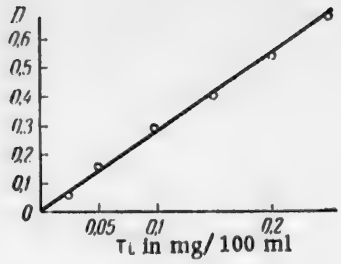

Fig. 2. Relation between the color of the titanium complex with arsenazo and the titanium concentration of the solution at pH 2,5-3.

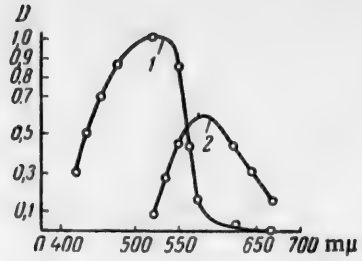

Fig. 3. Light absorption curves of the complex of titanium and arsenazo: 1) Reagent 2) titanium complex.

TABLE 1

Determination of Titanium with Arsenazo (in mg)

Ti taken, mg	Ti found, mg	
0.01	0.01	0.012
0.06	0.06	0.058
0.10	0.10	0.105
0.12	0.12	0.13
0.16	0.17	0.155
0.20	0.21	0.21
0.25	0.25	0.24

The photometric method of determining titanium with arsenazo has been successfully used for determination of large amounts of titanium in titanium metal and in two samples of titanium and chromium boride (Table 3).

Analytical Procedure. 0.2 g of titanium boride, titanium metal, or the double boride of titanium and chromium is dissolved in 20 ml of sulfuric acid (1:1) containing 7 ml of hydrogen peroxide. The latter is added until the titanium boride has dissolved completely. The solution is heated until white fumes are evolved; during this stage the solution is decolorized and the hydrogen peroxide is decomposed. The solution is poured into a 100 ml standard flask. When an insoluble residue remains, this is filtered off, washed, and then fused with potassium pyrosulfate, the solution of the melt obtained is combined with the main solution and the volume made up to the mark with water. 5 ml of this solution is measured out into a 200 ml standard flask in which it is diluted to the mark with water and thoroughly mixed. By this means the requisite pH is obtained. 5 ml of this solution in the

TABLE 2

Effect of Masking Agents

Masking agent	Concentration g/ml	Titanium taken, mg	Optical density of the complex with arsenazo
—	—	0.125	0.38
Hydrofluoric acid	0.0002	0.125	0
Oxalic "	0.025	0.125	0
Tartaric "	0.125	0.125	0.34
Citric "	0.0125	0.125	0.36

TABLE 3

Determination of Titanium in Borides and Titanium (sample weight 0.2 g)

Test material	Titanium, %		Iron content %
	amount present*	amount found	
Titanium metal	97,0	97,2	3,0
	97,0	97,2	3,0
	97,0	96,5	3,0
	97,0	96,5	3,0
	97,0	97,4	3,0
Titanium boride	66,6	66,9	2,0
	66,6	66,5	2,0
	66,6	66,9	2,0
	66,6	66,6	2,0
	57,10	57,3	1,5
	57,10	57,5	1,5

*Determined by the cupferron method.

200 ml flask is measured out into a 100 ml flask and 10 ml of arsenazo solution added, the volume is made up to the mark with water and the whole mixed; the optical density is measured in a cuvette with a layer thickness of 20 mm, an orange filter being used (6-FÉK-N). The amount of titanium in titanium boride is found by comparing the optical density of the solution obtained with the optical density of a solution of titanium metal containing a known amount of titanium, and prepared under similar conditions. The accuracy of the method is ± 0.4%.

SUMMARY

A quantitative method has been developed for the photometric determination of titanium with arsenazo; the latter forms with titanium a stable, soluble, violet colored compound at pH 2.5-3. The method permits the determination of 0.01 mg and more of titanium.

The method has been used for the determination of large amounts of titanium (up to 70%) in titanium boride.

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AN EXTRACTION PHOTOMETRIC METHOD FOR THE DETERMINATION OF THORIUM IN NATURAL MATERIALS

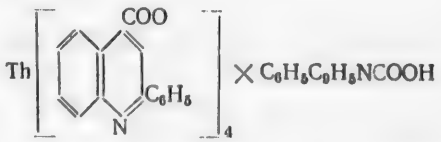
L. I. Gerkhardt

The reagent arsenazo which was suggested by V. I. Kuznetsov [1] for the determination of thorium and uranium, is widely used in various analytical methods [2, 3].

The basis of the method described here is the precipitation of thorium with phenylcinchonic acid (atophan), followed by its extraction as the phenylcinchonate with n-butanol from weakly acid solutions (pH 2.5-4.5), and its final determination with arsenazo in an aqueous-organic medium (acetone-butanol-water) in the presence of tartaric* and citric acids [4].

Precipitation of thorium at pH 2.5-4.5 was carried out with a tenfold excess of 2% aqueous solution of ammonium phenylcinchonate, the latter was prepared as follows [7]. 2 g of phenylcinchonic acid was treated with 10% ammonia solution in a porcelain basin, and heated on a water bath until the odor of ammonia had dissappeared. The dry residue was dissolved in 100 ml of water or butanol.

The chemical composition of thorium phenylcinchonate was established on the basis of the difference between the amount of phenylcinchonic acid which reacts with the thorium ions, and the free acid found by titration with 0.1 N sodium hydroxide in the presence of phenolphthalein [7]. The results obtained show that the composition of thorium phenylcinchonate corresponds to the formula:



The extractability of thorium phenylcinchonate with amyl acetate, n-butanol, isoamyl alcohol, acetylacetone, methyl butyl ketone, and chloroform was studied (Table 1).

It is evident from Table 1 that butanol and amyl acetate extract thorium quantitatively; butanol was used as the extracting agent.

Extraction of thorium phenylcinchonate with butanol is possible in the pH range 2.5-4.5 (Fig. 1). The pH of the test solutions was established by means of 0.09 N hydrochloric acid and 1 M ammonium acetate solution. Into the solution containing thorium ions (Table 2) was added 2 ml of 1 M ammonium acetate solution and 0.09 N hydrochloric acid up to 10 ml; the pH of such a solution was 3-4. Thorium was then extracted with an equal volume of a 1% solution of ammonium phenylcinchonate in butanol. To the extract, after its removal from the aqueous phase, was added 5 ml of acetone, and 3 ml of 0.05% arsenazo solution in 0.09 N hydrochloric acid, and the volume made up to 25 ml with 0.09 N acid; the whole was mixed and the optical density measured in 30 ml cuvettes on a FÉK-M photocolorimeter using a yellow-green filter (570 mμ), relative to a zero solution containing the same reagents.

*Determination of thorium with thoron in the presence of tartaric acid has been described in [6].

TABLE 1

Distribution of Thorium between the Organic and Aqueous Phases in %

Extracting agent	Distribution		Partition coefficient
	extracting agent	water	
Amyl acetate	100	0,00	—
Butanol	100	0,00	—
Isoamyl alcohol	91,76	8,24	11,13
Acetylacetone	80,08	19,92	4,02
Methyl butyl ketone	31,51	68,49	0,46
Chloroform	6,21	93,79	0,07

The amount of thorium was determined by means of a calibration curve which was constructed in similar fashion, using solutions containing 10, 15, 20, and 70 γ of thorium in 25 ml of the aqueous organic solution.

Thorium is quantitatively extracted from hydrochloric acid solutions at a pH of 2.5-4.5 by means of butanol (Table 2).

Solutions of the complex of thorium with arsenazo in the aqueous organic medium are more stable than solutions of this complex in water [2, 3, 5]; the optical density of such solutions remains unchanged for several days. The maximum light absorption of the aqueous organic solutions of the thorium arsenazo complex is located at 570-575 mμ (Fig. 2) just as that of the aqueous solutions. The molar extinction coefficient of the thorium arsenazo complex, as found by the saturation method [8, 9] at several wavelengths, is equal to 29000 at 570 mμ.

In order to study the relation between the optical density of the thorium arsenazo complex and the pH of the solution in an aqueous organic medium, 3 ml of 0.05% arsenazo solution and the appropriate amount of 1 M ammonium acetate were added to 1 ml of thorium solution (28 γ Th). The pH was controlled potentiometrically. The optical density was measured on a FÉK-M photocolorimeter at 570 mμ.

From Fig. 3 it is clear that on increasing the pH from 0.5 to 1.5, the optical density also increases; afterwards, up to pH 2.5, the optical density remains constant. Complete complexing of the thorium occurs at pH 1.5, this indicates the high stability of the complex.

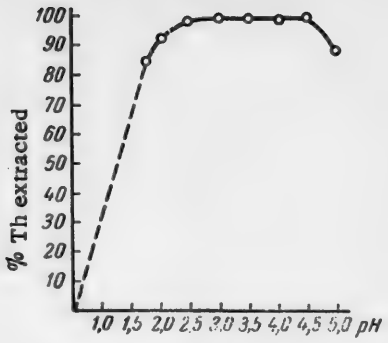
The relation between the light absorption of the thorium arsenazo complex and hydrogen ion concentration was determined. The optical density of a solution of the thorium arsenazo complex was measured on a SF-4 spectrophotometer at various wavelengths, at a layer thickness of 10 mm. The maximum light absorption, starting at pH 1.5 right up to 2.5, was found at 570 mμ (Fig. 4).

The effect of the amount of arsenazo on the optical density of the thorium arsenazo complex in an aqueous organic medium was studied. On measuring the optical density of the complex in comparison with a solution of

TABLE 2

Determination of Thorium in Pure Solutions, γ

Taken	Found	Error
4.83	4.5	-0.33
19.34	19.5	+0.16
18.0	18.0	0.00
28.6	28.5	-0.10



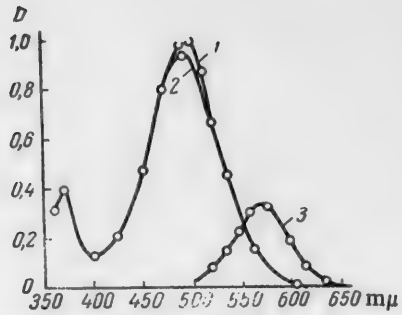


Fig. 1. Effect of pH on the extraction of thorium by n-butanol.

Fig. 2. Light absorption of solutions of arsenazo I and of the complex of thorium with arsenazo (concentration 2.9×10^{-5} M, SF-4 cuvette 10 mm). 1) Arsenazo in an aqueous organic medium; 2) the thorium arsenazo complex in an aqueous organic medium; 3) the thorium arsenazo complex plus arsenazo in an aqueous organic medium.

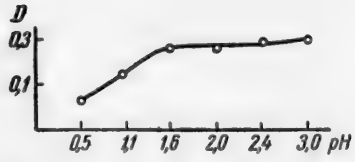


Fig. 3. Effect of pH on the optical density of the thorium arsenazo complex (570 mμ).

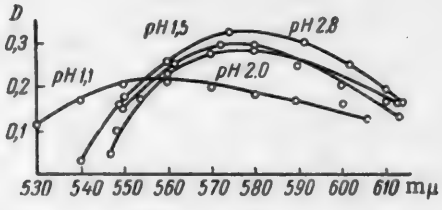


Fig. 4. Light absorption of the thorium arsenazo complex as a function of the ph of the medium.

the reagent in an aqueous organic medium at 570 mμ and at a pH of 1.5-2.0, it was established that the highest optical density is found in the presence of two milliliters of 0.05% arsenazo solution (Fig. 5). A further increase in the amount of the arsenazo solution did not alter the optical density of the solution.

The composition of thethorium complex with arsenazo in an aqueous organic medium was established by the isomolar series method [10, 11]. The maximum on the curve composition–optical density corresponds to a molar ratio of thorium to arsenazo of 1:1 (Fig. 6). These results were also confirmed by the method of the ratio of the slopes of the curve [12] (Fig. 7). For this purpose two series of solutions were prepared, one of which had differing concentrations of thorium in the presence of a constant excess of reagent, while the other had a constant concentration of thorium for variable concentrations of reagent, expressed in moles per liter. The optical density was measured at 570 mμ. The results given in Fig. 7 confirm that the ratio of thorium to arsenazo in the complex is 1:1.

In order to determine thorium in the presence of titanium and zirconium, ascorbic acid (1-2 mg) was added to the test solution, followed by 2 ml of 1 M ammonium acetate solution, and the volume made up to 10 ml with 0.09 N hydrochloric acid; this solution was extracted with an equal volume of a 1% solution of ammonium phenylcinchonate in butanol. After removing the extract from the aqueous phase, it was dissolved in 5 ml of acetone, 3 ml of a 0.05% arsenazo solution prepared in 0.09 N hydrochloric acid was added, this was followed by 0.5 ml of 10% tartaric acid, and 3-5 mg of ascorbic acid, and the optical density measured as described above.

Ascorbic acid in this medium forms with titanium a complex compound which is not extracted by butanol. Zirconium and titanium (Table 3) are not quantitatively extracted with butanol in the presence of ascorbic acid. During extraction of thorium as its phenylcinchonate by means of butanol, traces of titanium and zirconium pass into the extract, but interference on their part is prevented by addition of tartaric and ascorbic acid.

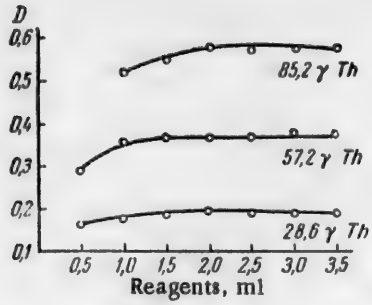


Fig. 5. Effect of the amount of reagent on the optical density of the thorium arsenazo complex.

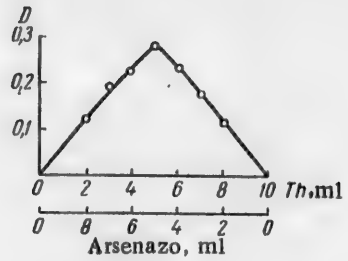


Fig. 6. Determination of the composition of the thorium arsenazo complex by the isomolar series method.

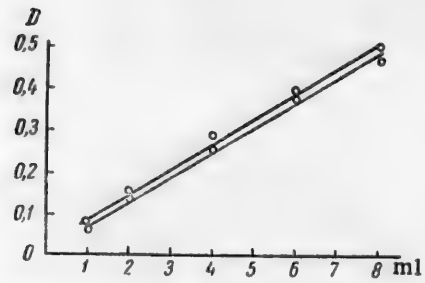


Fig. 7. Determination of the composition of the thorium arsenazo complex by the method of the ratios of the slopes of the curves.

TABLE 3

Distribution of Zirconium and Titanium in the Presence of Ascorbic Acid

Amt. in mg/10 ml		Distribution, mg			
		Zr		Ti	
Zr	Ti	butanol	water	butanol	water
1,0	—	0,40	0,60	—	—
1,0	—	0,40	0,60	—	—
1,0	—	0,30	0,70	—	—
1,0*	—	1,00	0,00	—	—
—	1,0	—	—	0,05	0,95
—	1,0	—	—	0,10	0,90
—	1,0	—	—	0,03	0,97
—	1,0*	—	—	0,90	0,10

*Ascorbic acid not added.

It is clear from Table 4 that thorium can be determined in the presence of titanium and zirconium by the given method with a permissible error.

The effect of iron and uranium during the extraction-photometric determination of thorium was studied under the same conditions. Ascorbic acid reduces iron (III) to the divalent state which does not interact with phenylcinchonic acid; uranium (VI) gives a colores complex compound with ascorbic acid [13], and, just like titanium, is not extracted with butanol. In addition, uranium (VI) forms a colored complex with arsenazo in neutral media. In acid media (pH < 4) uranium does not interfere.

The results given in Table 5 indicate that it is possible to determine thorium in the presence of iron.

Ions of uni- and divalent metals (Na^+, Ca^{2+}, etc.) do not interact with phenylcinchonic acid, and are not extracted with butanol; trivalent elements, including the rare earth element [14], vanadium, molybdenum, and tungsten, in the presence of ascorbic acid, do not give phenylcinchonates either, and are not extracted with butanol.

It is clear from Table 7 that I, II, and III group elements, and also vanadium, molybdenum, and tungsten do not affect thorium determination.

A Method for Determining Thorium in Ores and Minerals

Five to fifty mg of ore or mineral was fused in a porcelain crucible with 1.5-2 g of sodium peroxide, in a muffle at 550°, until a homogeneous melt was obtained. The cooled melt was dissolved in 30 ml of water; after heating for 10-15 minutes the precipitate was filtered off, washed 2-3 times with cold water, and then dissolved on the filter paper in 5-10 ml of 5% (by volume) of hot hydrochloric acid; the solution was neutralized with ammonia to a pH of 2.5-3.0 (congo red paper); the solution was then transferred into a 25 ml standard flask, in which its volume was made up to the mark with 0.09 N hydrochloric acid.

TABLE 4

Determination of Thorium in the Presence of Titanium and Zirconium

Amount taken in 10 ml			Th found, γ	Error in determining Th, γ
Ti, mg	Zr, mg	Th, γ		
0.5	0.5	4.8	4.5	-0.3
1.0	1.0	18.0	18.5	+0.5
1.0	1.0	18.0	18.5	+0.5
1.0	1.0	18.0	19.5	+1.5
1.0	1.0	18.0	17.0	-1.0

TABLE 5

Determination of Thorium in the Presence of Iron

Amount taken in 10 ml		Th found, γ	Error in determining Th, γ
Th, γ	Fe, mg		
14.0	20.0	12.5	-1.5
21.8	40.0	22.5	+0.7
21.8	100.0	20.5	-1.3
21.8	120.0	23.0	+1.2
14.0	140.0	12.5	-1.5

TABLE 6

Determination of Thorium in the Presence of Uranium (2.18 γ Th and 1 mg U in 10 ml taken)

Th found, γ	Error in Th, γ	Th found, γ	Error in Th, γ
23.75	+1.95	21.25	-0.55
21.25	-0.55	23.75	+1.95
21.25	-0.55	21.25	-0.55

An aliquot of this solution (2-10 ml) was transferred into a 20-50 ml separatory funnel, 1-2 mg of ascorbic acid and 2 ml of 1 M ammonium acetate were added and the volume made up to 10 ml with 0.09 N hydrochloric acid. The solution was thoroughly mixed, and 5 ml of a 2% solution of ammonium phenylcinchonate in butanol added, this was followed by 5 ml of butanol and the thorium than extracted for 20-40 seconds. After the layers had separated, the extract was transferred to a 25 ml standard flask and the funnel rinsed out with 5-10 ml of acetone which was mixed with the extract, 3 ml of a 0.05% arsenazo solution was then added, followed by 1-5mg of ascorbic acid, and 0.5 ml of 10% tartaric acid, the volume was finally made up to the mark with 0.09 N

TABLE 7

Determination of Thorium in the Presence of Various Ions (28.6 γ of Th taken)

Metal ions, mg/10 ml	Th found in the extract, γ	Error in Th, γ	Metal ions, mg/10 ml	Th found in the extract, γ	Error in Th, γ
Na^+ 5,0	28,8	+0,2	Zn^{2+} 5,0	29,0	+0,4
Ag^+ 5,0	28,3	—0,3	Fe^{2+} 3,0	27,5	—1,1
Cu^{2+} 3,0	29,0	+0,4	Al^{3+} 5,0	28.3	—0,3
Mg^{2+} 3,0	28,5	—0,1	La^{3+} 1,3	28,5	—0,1
Ca^{2+} 3,0	27.5	—1,1	Total 2,0	29,0	+0,4
Mn^{2+} 4,0	28,0	—0,6	VO_3^- 4,0	28,8	+0,2
Ba^{2+} 3,0	28,3	—0,3	MoO_4^{2-} 3,0	28,2	—0,4
Ni^{2+} 1,5	29,0	+0,4	WO_4^{2-} 3,0	28,6	0,0

TABLE 8

Determination of Thorium in Ores and Minerals, %

Main components		Found by the given method	Found by method [15]	Error (relative)
ZrO_2	6,21	0,13; 0,113	0,12	+0,8
TiO_2	6,00			
Fe_2O_3	55,67			
Al_2O_3	12,0			
V_2O_5	0,24			
ZrO_2	8,28	0,172; 0,15	0,16	+0,6
Total	2,10			
ZrO_2	7,32	0,19	0,19	0,00
Total	2,27			
ZrO_2	9,90	0,133; 0,141	0,14	—2,1
Total	0,97			
R_2O_3	31,9	0,17; 0,18	0,17	+3,0
ZrO_2	6,0			
TiO_2	1,68			
	Zircon	0,005	0,059	—15,0
	Pyrochlor	1,67	1,66	+ 0,6
	Ore	0,005	0,006	—16,0

hydrochloric acid. After 1-2 hours the optical density was measured on a FÉK-M photocolorimeter in 30 mm cuvettes at 670 mμ (with a yellow-green filter). When such a filter is not available it is necessary to combine a green filter with a liquid filter. A saturated solution of potassium dichromate can be used as the liquid filter, the dichromate being placed in a 10mm cuvette in the path of the light rays.

The amount of thorium was determined on the basis of a calibration curve which was constructed as follows: 0—5—10—15—70 γ of thorium was extracted with ammonium phenylcinchonate in butanol. The extracts were transferred into 25 ml standard flasks, 5 ml of acetone, 3 ml of 0.05% arsenazo, 1-5 mg of ascorbic acid, and 50 mg of tartaric acid were added to each flask and the volume made up to the mark with 0.09 N hydrochloric acid. The optical density was measured under the same conditions.

SUMMARY

A study has been made of the conditions for separating thorium from accompanying elements by extracting thorium phenylcinchonate with n-butanol at a pH of 2.5-4.5 in the presence of ascorbic acid.

It has been established that it is possible to determine thorium photometrically on the basis of its complex with arsenazo in the presence of tartaric and ascorbic acids in a medium of acetone–butanol–water.

An extraction-photometric method has been developed for the determination of thorium in ores and minerals by means of arsenazo I; this method permits determination of 0.005% to whole parts of a percent of thorium on small aliquots of sample, with a relative error of 5-20%.

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COMPLEXONOMETRIC AND PHOTOMETRIC DETERMINATION OF THORIUM IN MINERALS AND ORES

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Large amounts of thorium (> 1-2%) are determined in monazite and other minerals and ores mainly by the iodate titrimetric method [1], or by gravimetric methods using fluoride, oxalate, and certain other anions as precipitants [2]. These methods require large aliquots of test material, repeated precipitations of the precipitates, and a determination takes 3-4 working days. Methods were published recently for the complexonometric determination of thorium using metalloindicators: pyrocatechin violet [3], alizarin [4, 5], chromazurol [6], cacothelin with Fe^{2+} [7], 2, 7-dinitroso-1, 8-dihydroxynaphthalene-3, 6-disulfonic acid [8], eriochrome cyanine [9], 1-(2-pyridylazo)2-naphthol [10] and some others.

The practical value of these indicators is not very high, particularly when applied for the analysis of mineral raw materials. The color change of the indicator at the endpoint is only clearly manifested during titration of thorium in pure solutions.

The aim of the work described here was to develop a rapid and convenient complexonometric method for the determination of large amounts of thorium, and the use of arsenazo [13] and a photometric method for the determination of small amounts of thorium in minerals and ores [11, 12].

First, a study was made of the conditions necessary for the complexonometric titration of thorium in solutions containing calcium and also titanium, zirconium, and the rare earths, using ferric thiocyanate as the indicator.

Thorium was titrated in the presence of calcium by the following method. To 20-25 ml of a hydrochloric acid solution containing thorium and calcium in the amounts indicated in Table 1, at a pH of 2-3, (congo red paper) was added 1 ml of a 30% solution of potassium (ammonium) thiocyanate, and 3-4 drops of ferric chloride solution, containing 0.1 mg of iron per ml; the final solution was heated to 60° and slowly titrated with 0.002 M Complexon III (EDTA) solution until the color disappeared on addition of one drop of solution.

Into another flask containing 20 ml of water was introduced 1 ml of thiocyanate solution, 2 drops of hydrochloric acid 1:1, and 3-4 drops of ferric chloride solution. This solution was also titrated until the color disappeared. From the number of mls of 0.002 M Complexon III solution used for titrating thorium and iron, the number of ml of this solution used for titrating iron was subtracted. One ml of Complexon III solution corresponded to 0.464 mg of thorium.

It is clear from Table 1 that calcium does not interfere with the complexonometric titration of thorium.

It is evident from Table 2 that zirconium and titanium, just like thorium, are titrated by Complexon III. During titration of thorium with Complexon III in the presence of ferric thiocyanate as indicator, a sharp change is observed at the end point (conversion of iron into the complexonate). The rare earths form stable compounds with Complexon III in a weakly alkaline medium. It is clear from Table 3 that the rare earths do not interfere with the titration of thorium.

In order to remove thorium from accompanying elements, the iodate-tartrate [11], and the acetonedioxalate method [12] were used. Thorium was separated from the greater part of the zirconium and titanium by the iodate-tartrate method; subsequently, in addition, for the quantitative removal of thorium from titanium and zirconium, thorium was precipitated with acetonedioxalic acid.

TABLE 1

Determination of Thorium in the Presence of 50 mg Calcium

Th taken, mg	0.002 M Complexon III solution used, ml	Th found, mg	Absolute error, mg
3.953	8.50	3.944	-0.009
3.953	8.30	3.851	-0.102
3.953	8.40	3.898	-0.055
1.977	4.00	1.856	-0.021
1.977	4.30	1.995	+ 0.018

Decomposition of Test Material and Preparation of the Solution for Precipitation of the Thorium. 5.00-50.00 mg of test material was placed in a 10 ml porcelain crucible containing about 1 g of sodium peroxide and 4-5 mg of ferric oxide; 1-2 g of sodium peroxide was added and the mass fused in a muffle at 550° until a homogeneous melt was obtained (2-3 minutes). The cooled melt was treated with 50-80 ml of water at 100° for 10 minutes; after 25 minutes, the solution was filtered through a 7 cm diameter "white band" filter paper, and washed 2-3 times with a 0.5% solution of sodium hydroxide. The metal hydroxides were dissolved on the filter in 9 ml of hot nitric acid 1:2, and 10 ml of hot water. The filter was washed with 5-6 ml of hot water. 1 drop of hydrogen peroxide was added and the solution cooled to 1-5°, thorium was then precipitated with iodate in the presence of tartaric acid and hydrogen peroxide.

Iodate Precipitation. To the solution was added 5 ml of a 60% solution of tartaric acid, 0.5 ml of a 3% solution of mercury nitrate, and 10 ml of a 6% solution of potassium iodate, the volume was made up to 50 ml with water and the whole thoroughly mixed. When the test material contained an appreciable amount of thorium, zirconium, and titanium a large precipitate of the metal iodates was formed. When only small amounts of these elements were present the solution merely became turbid.

At this stage of the procedure 50 ml of the solution should contain 3 ml of concentrated nitric acid (63-64%), 15 mg of mercury (II) in terms of the oxide, 3 g of tartaric acid, and 0.6 g of potassium iodate. The solution was left in a cool place for 45 minutes, after which the precipitate was filtered through a double "white band" filter paper 7 cm in diameter, using a filter aid (macerated filter paper). The filter was washed with 20-25 ml of a potassium iodate wash solution*. The precipitate on the filter was dissolved in 10-15 ml of 20% by volume, hot hydrochloric acid. The filter was washed 2-3 times with 10-15 ml of hot water. The filtrate was collected in the same beaker as that used for precipitating the thorium and then evaporated to a volume of one ml.

When the material contained large amounts of thorium, zirconium, and titanium, the oxalate precipitation was used (see below) in order to remove the thorium completely from zirconium and titanium: when only small amounts of thorium, zirconium, and titanium were present there was no need to resort to the oxalate precipitation. In the latter case, 5-6 ml of concentrated hydrochloric acid, and 5-6 drops formaldehyde solution were added the solution was then evaporated to a volume of 0.5 ml. This operation was repeated until the iodine had been removed. 6-8 ml of water was added and the pH adjusted to pH 2-3 with ammonia (congo red paper). 1% ascorbic acid solution was added until the solution was decolorized, 0.2 ml of the ascorbic solution was then added in excess. The solution was filtered into a 25 ml standard flask and the volume made up to the mark with 0.09 N hydrochloric acid, the solution was thoroughly mixed and the thorium determined photometrically [12].

Oxalate Precipitation. To the residue obtained after evaporating off the hydrochloric acid, 30-40 ml of water was added, followed by 0.5 ml of a 25% solution of calcium chloride, and sodium acetate solution dropwise

*500 ml of this solution contained 6 g of potassium iodate, 3 ml of hydrogen peroxide, and 30 ml of concentrated nitric acid.

TABLE 2

Determination of Thorium in the Presence of Zirconium and Titanium

Th taken, mg			0.002 M Complexon III solution used, ml	Th found, mg	Absolute error, mg
Th	Zr	Tl			
3,953	0,010	—	8,53	3,959	+0,006
3,953	0,030	—	8,62	4,000	+0,047
3,953	0,060	—	8,69	4,032	+0,079
3,953	—	0,010	8,54	3,967	+0,014
3,953	—	0,030	8,57	3,971	+0,018
3,953	—	0,050	8,69	4,032	+0,079
3,953	—	0,080	8,81	4,087	+0,134

TABLE 3

Determination of Thorium in the Presence of the Rare Earths

Taken, mg		0.002 M Complexon III solution used, ml	Th found, mg	Absolute error, mg
Th	total			
3,953	2,096	8,60	3,990	+0,037
3,953	5,200	8,50	3,944	—0,009
7,906	7,860	17,00	7,888	—0,018
3,953	12,620	8,50	3,948	—0,005
3,953	34,500	8,53	3,981	+0,028

TABLE 4

Complexonometric Titration of Thorium after its Removal from Accompanying Metals

Taken, mg					Th found, mg	Absolute error, mg
total rare earths	Fe	Tl	Zr	Th		
15,0	50,0	2,0	0,438	1,976	1,972	—0,004
8,0	50,0	1,0	1,449	7,906	8,004	+0,098
8,0	50,0	1,0	1,449	3,953	4,060	+0,107
8,0	25,0	1,0	1,449	3,953	3,944	—0,009
12,0	25,0	1,0	1,41	5,929	6,032	+0,103
12,0	75,0	2,0	2,41	7,906	7,842	—0,064
8,0	50,0	1,5	2,50	3,953	4,018	+0,065
8,0	50,0	1,5	2,50	5,929	5,915	—0,014
10,0	25,0	10,0	5,0	1,430	1,324	—0,106
10,0	3,0	5,0	35,0	1,430	1,370	—0,060
10,0	3,0	3,0	25,0	2,840	2,900	+0,060
10,0	1,0	27,0	5,0	1,430	1,400	—0,030
10,0	1,0	21,0	5,0	2,840	2,790	—0,050

until the pH was 5 (congo red paper). The volume of the solution was made up to 50 ml with water and 7.5 ml of solution of acetonedioxalic acid added; the subsequent procedure followed was that described in [12]. Thorium was determined complexonometrically or photometrically in the solution obtained.

TABLE 5

Photometric Determination of Thorium after Its Separation from Accompanying Metals by the Iodate and Oxalate Methods

Taken, mg					Th found, mg	Absolute error, mg
total rare earths	Fe	Ti	Zr	Th		
10	2,0	—	31	0,020	0,018	—0,002
10	3,0	1,0	24,0	0,012	0,015	+0,003
10	25,0	10,0	10,0	0.050	0,044	—0,006
10	12,0	22,0	1,0	0.100	0,097	—0,003
10	12,0	16,0	—	0,208	0,195	—0,013
10	6,0	30,0	5,0	0,343	0,358	+0,015

TABLE 6

Complexonometric Determination of Thorium in Natural Materials

Designation of material	Thorium found (%) by:		Error (relative), %
	complexonometric method	control method	
Monazite I	2,31; 2,18	2,20	+2,2
The same II	1,72; 1,67	1,70	0,0
" " III	6,76; 6,54	6,44	+3,3
" " IV	3,20	3,28	—2,5
" " V	9,61; 9,88	9,80	+0,5
" " VI	2,55	2,65	+4,0
Winkite 1	0,69	0,68	+1,5
The same 2	1,28	1,32	—3,0
" " 3	1,44	1,35	+6,0
Zircon I	1,70	1,73	+1,8
The same II	1,36	1,30	+4,6
Ferrithorite	12,37	12,00	+3,0
Klopinite	2,56; 2,36	2,44	+0,8

Complexonometric and Photometric Method of Determining Thorium. To 10-15 ml of the test solution was added 1 ml of a 30% solution of potassium thiocyanate (ammonium). In the presence of iron the color of ferric thiocyanate appears; this acts as an indicator during titration.

In another 50 ml flask a compensating solution was prepared. For this purpose, the same amount of water was added, followed by 2 drops of hydrochloric acid, and 1 ml of potassium thiocyanate (ammonium).

To the compensating solution was added 3 drops of ferric chloride solution (10 mg Fe in 100 ml). When the color of the ferric thiocyanate was more intense in the test solution, 1-2 drops of 0.001% ascorbic acid solution was added, and the colors of the solutions compared after 2-3 minutes.

The color of both solutions should be exactly the same; when the color differed, 1-2 drops of ferric chloride solution was added to the less intensely colored solution.

First the iron in the compensating solution was titrated with 0.002 M (or 0.005 M) Complexon III solution. This solution was heated to 60° and then titrated slowly, dropwise, until it was colorless. The buret reading gave the correction to be applied. The test solution was also heated to 60° and slowly titrated with 0.002 M Complexon III solution until it was colorless. Titration was repeated twice.

It is clear from Tables 4 and 5 that complexonometric titration of thorium, and its photometric determination after its removal from accompanying elements by the iodate and oxalate methods, give satisfactory results.

TABLE 7

Colorimetric Determination of Thorium in Minerals and Ores

Test material	Thorium found (%) by		Error (relative), %
	given method	control method	
Ore (ZrO_2—6,0, TiO_2—8%)	0,13	0,12	+ 8,3
Ore (ZrO_2—8,0)	0,14	0,14	0,0
Silicate ore	0,01;0,009	0,01	0,0
The same	0,007	0,007	0,0
Zircon	0,12; 0,13	0,12	+ 4,0
Ilmenite	0,04	0,036	+11,0
Winkite 1	0,68	0,69	— 1,30
The same 2	1,32	1,28	+ 3,1
" " 3	1,36	1,44	— 6,0
Monazite	3,28	3,20	2,2

During the complexonometric determination of thorium in thorium minerals—monazites from various deposits, ferrothorite, winkites, and also in ores—the solutions should be freed even from traces of zirconium (test with alizarin in a strongly acid medium) and titanium (test with hydrogen peroxide).

The method gives completely satisfactory results (Table 6).

Photometric determination of thorium was carried out on materials with a complex composition, containing from 0.005 to 3-4% of thorium and up to 60-70% of zirconium and titanium. The determination was carried out by means of arsenazo in tartaric acid* by a method described earlier (Table 7).

SUMMARY

A study has been made of the complexonometric titration of thorium in solutions containing calcium, zirconium, titanium, and the rare earths, using ferric thiocyanate as indicator.

A titrimetric method has been developed for the determination of thorium in natural materials containing large amounts of zirconium and titanium, in which use is made of the iodate and oxalate methods of precipitation, and also of a colorimetric method for the determination of small amounts of thorium by means of arsenazo. Determination of thorium by these methods takes 8-12 hours.

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COMPLEXONOMETRIC DETERMINATION OF MOLYBDENUM AFTER ITS REDUCTION TO THE QUINQUEVALENT STATE

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Quinquevalent molybdenum reacts with disodium ethylenediamine-tetracetate (Complexon III) in the molar proportions of 2:1 [1]. The compound thereby formed has been prepared, and its composition established by analysis and by a photometric method. Our experiments have shown that the readily hydrolyzable quinquevalent molybdenum does not form a precipitate in the presence of excess Complexon III, even in a strongly alkaline medium. On titrating the excess Complexon III with a solution of a zinc salt in the presence of chromogen black ET, a distinct color change is observed at the endpoint, and the color does not change on standing in air. All this indicates that the compound of quinquevalent molybdenum and Complexon III has a high stability.

We have shown previously [2] that the accuracy of the direct complexonometric titration of sexivalent molybdenum in the presence of pyrocatechol and indigocarmine as indicator, amounts to 2%; the color change at the endpoint is not clear enough, so that it is difficult in practice to titrate sexivalent molybdenum directly with Complexon III solution.

A review of complexonometric methods for the determination of sexivalent molybdenum is given in one of our previous articles [2].

The aim of the work described here was to establish the pH limits for the formation of the compound of quinquevalent molybdenum with Complexon III, and to establish the possibility of an indirect complexonometric determination of molybdenum after its conversion into the quinquevalent state.

A zinc or magnesium salt was used for determining the excess Complexon III.

EXPERIMENTAL

A solution of ammonium molybdate (chemically pure, GOST 3765-53) in water was standardized by the 8-hydroxyquinoline method [3]. 1 ml of this solution was found to contain 1.898, 1.890, 1.898, 1.891, and 1.886 mg of Mo (an average of 1.893 mg Mo/ml).

The Complexon III was purified by Bleadel and Knight's method [4], methanol being used instead of ethanol. An accurate aliquot of this material dried to constant weight was dissolved in water in a standard flask. The concentration of the solution was checked by means of solutions of zinc, cadmium, and magnesium of known concentration [5]; according to the results obtained, the molarities obtained were 0.008045 M according to Cd, 0.008050 M according to $MgSO_4$, and 0.008035 M and 0.008050 M with respect to Zn; the average value was 0.008050 M.

Hydrazine hydrochloride was used without further purification for reducing sexivalent molybdenum. Other reducing agents proved to be less suitable.

The indicator was prepared by triturating one part of chromogen black ET with 200 parts of sodium chloride. A buffer solution with a pH of 10 was prepared by adding 70 g of ammonium chloride to 570 ml of a concentrated ammonia solution (sp. gr. 0.90) and diluting to 1 liter with water [5].

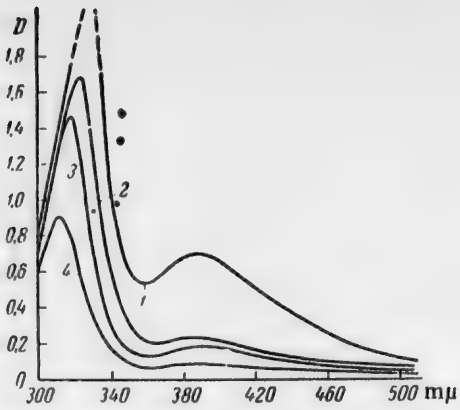

Fig. 1. Absorption curves for solutions of a quinquevalent molybdenum salt, and of the compound of quinquevalent molybdenum with Complexon III. SF-4 spectrophotometer. Cuvette with a layer thickness of 1 cm. All the curves were taken relative to water. 1) Mo^V ($4.032 \cdot 10^{-3}$ M) + Complexon III ($4.044 \cdot 10^{-3}$ M) in 0.24 M HCl, pH 2.17-9.30; 2) Mo^V ($4.032 \cdot 10^{-3}$ M) in 0.24 M HCl, Mo^V ($4.032 \cdot 10^{-3}$ M) + Complexon III in 2.0 M HCl; 3) Mo^V ($1.008 \cdot 10^{-3}$ M) + Complexon III ($1.011 \cdot 10^{-3}$ M) in 0.48 M HCl; 4) Mo^V ($1.008 \cdot 10^{-3}$ M) in 0.48 M HCl.

TABLE 1

Molar Extinction Coefficients of the Compound of Mo^V with Complexon III at Various Acidities (Determined at 387.5 mμ. Calculated on the basis of the Molar Concentration of Mo)

Acidity of the sol., pH	Molar coefficient	Acidity of the solution, M HCl	Molar coefficient
9,30	108		
9,08*	116	0,24	120
9,10*	115	0,24	115
8,70*	108	0,48	115
7,89	115	0,48	116
7,81	115	0,48	111
6,80	116	0,75	92
5,33	116	0,96	64
2,67	119	1,44	14
1,81	115	1,92	4,5
1,48	117		

*Solution obtained on standing in all cases of determination of quinquevalent molybdenum indicated.

Acidity Limits for the Formation of the Compound of Quinquevalent Molybdenum with Complexon III. The acidity limits within which the compound of quinquevalent molybdenum and Complexon III is formed, were established by a photometric method.

When excess Complexon III is added to the brownish-yellow solution of quinquevalent molybdenum, the solution becomes a bright green, both in acid and alkaline media. This leads one to suppose that the complex compound of quinquevalent molybdenum is formed over a wide range of acidities.

The absorption curves for the quinquevalent molybdenum salt $(NH_4)_3MoOCl_6$ on its own, and for the compound of quinquevalent molybdenum with Complexon III, at varying acidities of the solution, are shown in Fig. 1. The curve for $(NH_4)_3MoOCl_6$ has two maxima: one—the larger one—at 310 mμ, the other—the smaller—at 375 mμ. Curve 1 also has two maxima, but their heights are somewhat greater (for the same concentration of quinquevalent molybdenum), the maxima in this case being shifted towards the longer wavelengths; one is located at 317.5 and the other at 387.5 mμ.

At a hydrochloric acid concentration of 2.0 M HCl, in the presence of excess Complexion III, the absorption curve almost coincides completely with the absorption curve of the solution of the quinquevalent molybdenum salt (Fig. 1, Curve 2).

Thus, in 2.0 M HCl, quinquevalent molybdenum does not form a compound with Complexon III. In order to establish with greater accuracy the acidity limits within which formation of the complex with Complexon III occurs, the molar extinction coefficients of quinquevalent molybdenum in the presence of excess Complexon III were determined at various acidities. 19.34 mg of sexivalent molybdenum was reduced to the quinquivalent state as described below (during this operation the volume is reduced by one half). To the solution with the highest concentration of acid was added 20 ml of 0.01 M Complexon III solution, and the acidity adjusted to the requisite level by addition of hydrochloric acid or ammonia; the solution was then boiled, after cooling, its volume was made up to 50 ml with water and its pH measured by means of a pH meter with a glass electrode, or a calculated amount of acid was added. For acidities ranging from 0.24 to 2.0 M HCl, the zero solution used was a solution of a quinquevalent molybdenum salt of the same concentration at the corresponding acidity; while within the limits pH 1 to pH 9.30, a solution of a quinquevalent molybdenum salt with a pH of 1 was used, since at higher pH values hydrolysis of quinquevalent molybdenum occurs. These experiments showed that the optical densities of solutions of quinquevalent molybdenum differ little from each other at various acidities (for 19.34 mg of Mo^V in 50 ml, in 1 M HCl, D = 0.203; in 0.24 M HCl, D = 0.195; at pH = 1, D = 0.208). Thus

TABLE 2

Conditions for the Quantitative Reduction of Sexivalent Molybdenum by means of Hydrazine (18.93 mg Mo taken)

Conditions		Mo found, mg	Error	
			mg	%
HCl concentration, mole/liter	0,1*	—	—	—
	0,2**	18,60	— 0,33	— 0,74
	0,3	19,04	+ 0,11	+ 0,58
	0,4	18,85	— 0,08	— 0,42
	0,7	19,04	+ 0,11	+ 0,58
	1,0	19,12	+ 0,19	+ 1,00
	1,3	18,96	+ 0,03	+ 0,16
Amount of $N_2H_4 \cdot 2HCl$, mg	1	4,107	—14,82	—78,3
	5	16,15	— 2,78	—14,7
	10	18,88	— 0,05	— 0,26
	50	18,96	+ 0,03	+ 0,16
	100	18,73	— 0,20	— 1,06
	500	19,00	+ 0,07	+ 0,37
Duration of the reduction,*** minutes	0	12,28	— 6,65	—35,13
	1	16,65	— 2,28	—12,04
	2	18,85	— 0,08	— 0,43
	2	18,73	— 0,20	— 1,06
	5	19,00	+ 0,07	+ 0,37
	10	18,73	— 0,20	— 1,06
	30	18,96	+ 0,03	+ 0,16

*Molybdenum blue formed.

**Small amount of molybdenum blue formed.

***The time was counted from the moment when all the molybdate solution had been added to the hydrochloric acid solution of hydrazine. When this time had expired the reaction mixture was cooled with cold water.

measurement of the optical density of solutions at various pH values, relative to a null solution of a salt of quinquevalent molybdenum with pH 1 should not lead to a large error.

It is clear from Table 1 that on heating, quinquevalent molybdenum forms a compound with Complexon III within a wide range of acidities, namely from 0.5 M HCl to pH 10; within this range the reaction of complex formation proceeds quantitatively. Formation of a compound at such a high acidity could be of undoubted practical interest for the analytical chemistry of molybdenum were it possible to find a suitable complexonometric indicator, since most elements do not give a compound with Complexon III at such an acidity, and the reaction would appear to be selective.

As far as one can judge, quinquevalent molybdenum reacts with Complexon III fairly rapidly in hot acid solutions. At room temperature, in a medium of 0.5 M HCl, the reaction proceeds slowly.

For lack of an indicator for quinquevalent molybdenum it was complexonometrically determined by an indirect method at a pH of 10.

Conditions for the Reduction of Sexivalent Molybdenum to the Quinquevalent State by Means of Hydrazine. A study was made of the effect of acid concentration, the amount of hydrazine, and the duration of the reaction on the extent to which the sexivalent molybdenum is reduced.

The results (Table 2) show that the acid concentration during reduction should be higher than 0.3 M, otherwise, molybdenum blue is formed which interferes with titration. The amount of hydrazine hydrochloride should be greater than 10 mg per 40 ml of solution; when smaller amounts are used the sexivalent molybdenum is incompletely reduced. It is quite sufficient to boil the solution for 2 minutes.

When hydrazine is added to a cold, weakly acid solution of molybdate, or molybdate solution is added rapidly to a hot acid solution of hydrazine, molybdenum blue is formed which interferes with the titration. For

TABLE 3

Determination of Quinquevalent Molybdenum by Titration of Excess Complexon III with a Zinc Salt in the Presence of Chromogen Black ET-00

Mo, mg		Error		Mo, mg		Error	
in mg	%	in mg	%	in mg	%	in mg	%
113,6	113,1	—0,50	—0,44	18,9	18,9	0,0	0
75,72	75,58	—0,14	—0,18	18,9	18,9	0,0	0
75,72	75,56	—0,12	—0,16	18,9	18,8	—0,1	—0,43
37,86	38,07	+0,21	+0,55	9,46	9,56	+0,1	+0,97
37,87	38,24	+0,38	+1,00	9,46	9,38	—0,08	—0,86
37,86	37,94	+0,08	+0,21	3,79	3,95	+0,16	+4,4
28,40	28,54	+0,14	+0,49	1,89	1,80	—0,09	—4,7
28,40	28,34	—0,06	—0,21	1,89	2,05	+0,16	+8,4
18,9	19,0	+0,1	+0,4				

TABLE 4

Determination of Quinquevalent Molybdenum without Boiling (18.9 mg Mo taken)

Found, mg	Error		Found, mg	Error	
	in mg	in %		in mg	in %
18,1	—0,8	—4,2	18,7	—0,2	—1,1
18,3	—0,6	—3,2	18,7	—0,2	—1,2
17,7	—1,2	—6,2	18,6	—0,3	—1,6
18,7	—0,2	—1,1	18,6	—0,3	—1,7
18,7	—0,2	—1,1	18,5	—0,4	—2,4
18,6	—0,3	—1,6	18,3	—0,6	—3,2
18,8	—0,2	—0,9	17,9	—1,0	—5,3

reducing sexivalent molybdenum, it is best to add the test solution (10 ml) containing 10-100 mg of molybdenum, slowly, dropwise, to the hot, acid solution of hydrazine hydrochloride. When this technique is used no molybdenum blue is formed. Should some molybdenum blue still appear, further boiling will usually lead to its disappearance.

Determination of Quinquevalent Molybdenum by Titration with Complexon III, Excess of which is Determined by means of a Zinc Salt and Chromogen Black ET-00. After many preliminary experiments the following method was developed for determining molybdenum. In a 200 ml beaker is placed 2-5 ml of hydrazine hydrochloride solution (concentration 0.01 g/ml), and 1-3 ml of concentrated hydrochloric acid and the volume made up to 30 ml with water; the solution obtained is heated to the boil on an electric hotplate, when not more than 10 ml of the neutral or weakly acid test solution of molybdate, containing from 10 to 100 mg of Mo, is added, slowly, dropwise; boiling is continued for several minutes until the solution is yellow-brown in color. To this solution is added a known volume of 0.01 M Complexon III solution whose concentration is accurately known, and some of the mixture of chromogen black ET-00 with sodium chloride added on a spatula tip. The acid solution is neutralized with ammonia or NaOH until the yellow color of the solution changes to weak green; finally for each 100 ml of solution, 2 ml of the buffer solution with pH 10 is added, and the whole boiled. After cooling to 40-60° the solution should be bright green in color. If this is not the case a little more indicator should be added. The hot (40-60°) solution is titrated with 0.01 M zinc sulfate solution until the bright green color changes to red-brown on addition of one drop of titrant. For calculation it is assumed that quinquevalent molybdenum reacts with Complexon III in the molar ratio of 2 : 1.

Results of molybdenum determinations are given in Table 3. They show that the method has satisfactory accuracy. When this procedure is adopted, however, the conditions employed for reducing the sexivalent molybdenum must be strictly adhered to in order to avoid formation of molybdenum blue. If the latter should appear,

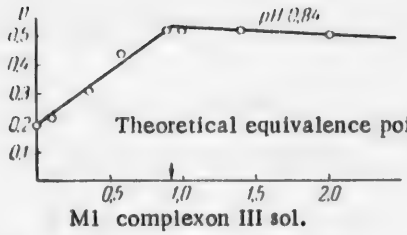

Fig. 2. Curves for the direct spectro-photometric titration of quinquevalent molybdenum with a solution of Complexon III, SF-4 spectrophotometer, cuvette with a layer thickness of 1 cm. Wavelength 387.5 mμ. 4.352 mg of M Mo^V taken; 0.915 ml of 0.02486 M Complexon III used. 4.365 mg of Mo found. The curves taken at pH 0.84, 1.15, and 1.80 almost coincided.

even if only in small amounts, the acidity of the solution should be raised and the solution boiled for a prolonged time, or even until the solution has been evaporated almost to dryness.

On neutralizing an acid solution of quinquevalent molybdenum containing excess Complexon III, a turbidity sometimes appears (as a result of the hydrolysis of Mo^V), this, however, disappears on heating.

Experiments showed that if the solution of quinquevalent molybdenum and excess Complexon III is not heated before titration, and is not titrated at 40-60°, then low results are obtained (Table 4).

Determination of quinquevalent molybdenum by titration of excess ComplexonIII with zinc sulfate solution in the presence of chromogen black ET-00 as indicator, takes a comparatively short time. It can be carried out in half an hour. The error in determining 10-100 mg of Mo is ± 0.5%, i.e., this method ensures slightly more accurate results than was possible by the direct titration of sexivalent molybdenum with Complexon III in the presence of pyocatechol and indigocarmine [2].

The test solution should be free from tartrates, citrates, oxalates, nitrates, and nitrites as well as other oxidizing agents. Iron interferes.

Small amounts of tungsten (10 mg of W per 40 ml) do not interfere with molybdenum determination. During reduction of molybdenum in the presence of tungsten a little of the blue compound is formed, but, on prolonged boiling in 0.7 M HCl a dirty blue compound is precipitated (contaminated tungstic acid) which dissolved in alkali. The blue compound disappears in the presence of excess Complexon III in an alkali medium on heating, and satisfactory results are obtained for molybdenum. When larger amounts of tungsten are present the blue compound does not disappear completely, and interferes with the titration. The results obtained are given in Table 5.

Elements which normally titrate with Complexon III in an alkali medium in the presence of chromogen black ET-00 interfere with molybdenum determination. In such cases total quinquevalent molybdenum and the accompanying elements can be titrated first, and then, in another aliquot of the test solution, the accompanying elements are titrated without reducing the sexivalent molybdenum (the latter, under the titration conditions used, does not form a stable compound with Complexon III); the amount of molybdenum is determined by difference. Results for such determinations are given in Table 5.

TABLE 5

Determination of Molybdenum in the Presence of Foreign Ions

Taken, mg	Mo, mg		Error		Taken, mg	Mo, mg		Error	
	taken	found	in mg	in %		taken	found	in mg	in %
5 W	9,46	9,32	—0,14	— 1,48	100 W*	9,46	7,91	—1,56	—16,4
10 W	9,46	9,46	—0,00	— 0,07	26 Zn	18,9	18,8	—0,1	— 0,69
20 W*	9,46	9,25	—0,21	— 2,29	13 Zn	18,9	18,9	+0,0	+ 0,10
20 W	9,46	8,96	—0,50	— 5,32	5 Mg	18,9	18,8	—0,1	— 0,42
40 W	9,46	8,17	—1,29	—13,6	16 Ca	18,9	19,0	+0,1	+ 0,53
100 W	9,46	7,41	—2,05	—21,6	12 Ni	19,2	19,5	+0,2	+ 1,25

*The volume of the solution during reduction was 80 ml.

In the presence of Mg, and Ca, titration should be carried out with $MgSO_4$ solution, while NaOH or KOH should be used instead of NH_4OH for neutralizing the solution. The chromogen black ET-00 indicator should be added before titration; the acid solution is best neutralized using universal indicator paper.

TABLE 6

Spectrophotocolorimetric Titration of Quinquevalent Molybdenum with Complexon III in an Acid Medium (4.35 mg Mo taken; wavelength 387.5 mμ)

pH of the solution being titrated	Found, mg	Error, mg	pH of the solution being titrated	Found, mg	Error, mg
0.43	–	–	1.15	4.36	+0.01
0.66*	4.41	+0.06	1.72	4.22	-0.13
0.84	4.36	+0.01	1.80	4.15	-0.20
1.15	4.29	-0.06	1.80	4.17	-0.18

*The optical density of the solution was measured after standing for a long time after addition of each new portion of Complexon III solution, since the reaction proceeds very slowly at pH 0.7.

Quinquevalent molybdenum can be determined by direct photometric titration with Complexon III solution in an acid medium at 387.5 mμ, by using a SF-4 spectrophotometer with a special cuvette having a layer thickness of 1 cm. The quinquevalent molybdenum solution was prepared as described above. The approximate pH value of the solution was measured with a pH-meter with a glass electrode. The volume of solution being titrated was 15 ml.

Although it has been established previously that even in 0.48 M HCl, Complexon III reacts quantitatively with quinquevalent molybdenum on heating, at such an acidity the titration cannot be carried out at room temperature, since the reaction proceeds slowly. It was established by photometric titration that at a pH of 0.66 the reaction finishes completely in half an hour, at a pH of 0.84 in 5 minutes, and at a pH of 1.80 in one minute. Direct titration at a pH > 2 is excluded since the quinquevalent molybdenum is hydrolyzed. Thus, direct titration of quinquevalent molybdenum is possible at pH 0.8-1.80. Under these conditions satisfactory results are obtained for molybdenum (Fig. 2, Table 6).

SUMMARY

The acidity limits within which the compound between quinquevalent molybdenum and Complexon III is formed have been established.

An accurate method has been developed for the determination of quinquevalent molybdenum, in which excess Complexon III solution is titrated with a zinc salt in the presence of chromogen black ET-00. It has been shown that it is possible to determine quinquevalent molybdenum by direct photometric titration.

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SPECTROPHOTOMETRIC STUDIES OF URANIUM SOLUTIONS

COMMUNICATION 2. A SPECTROPHOTOMETRIC METHOD OF DETERMINING URANIUM IN ORES AND OTHER MATERIALS AS THE THIOCYANATE AFTER EXTRACTION OF OF THE URANIUM WITH METHYL ETHYL KETONE*

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In a previous article [1] we have shown that direct determination of uranium on the basis of the value of the light absorption of uranyl nitrate in organic solvents is only applicable for fairly high concentrations of uranium. In order to increase the sensitivity of the determination of uranium, methods of extracting it in the form of inorganic and organic complexes [2-9] have been widely used. All the same, we think that it is better to start by extracting the uranium as its nitrate in an organic solvent (for separating it from most elements), and then determining it directly in the organic phase by a spectrophotometric method after addition of a suitable reagent. By using this technique, determination of uranium can be speeded up and simplified. After the work described here was completed (in 1954) a number of papers appeared which confirmed the advantages of such an approach for determining uranium [10-14].

We used methyl ethyl ketone for extracting uranyl nitrate; the partition coefficient of uranyl nitrate in this solvent is greater (K = 21) than in other organic solvents [1]. Ammonium thiocyanate was chosen as the reagent.

Measurements of the optical density were carried out on a SF-11 spectrophotometer using quartz cuvettes (layer thickness 1 cm) and were made relative to methyl ethyl ketone or a mixture of water and acetone containing all the reagents at the same concentrations as the test solution [15]. The uranyl nitrate solutions were prepared from high purity (99.7%) uranium metal. The uranyl sulfate was prepared from uranyl nitrate. Solutions of other salts were prepared from chemically pure or analytical grade reagents (the analytical grades were recrystallized). The methyl ethyl ketone and acetone were distilled.

Spectrophotometric Measurements of the Thiocyanate Complex of Uranium. In Fig. 1 (Curve 1) is shown the absorption curve of the uranium thiocyanate complex (2.1×10^{-4} M) in an aqueous acetone medium (60% acetone by volume). The molar absorption coefficients of the complex in this medium are: 6200, 3600, and 1300 at 350, 375, and 400 mμ respectively.

The effect of Fe, Cu, Al, Ti, V, and Mo (see also [16]) on the value of the light absorption of the uranium thiocyanate complex was studied. To a solution of uranyl sulfate, containing 0.5 mg of uranium, was added the sulfates of the elements listed above (V in the form of vanadate, Mo as the molybdate), 0.4 ml of 10% stannous chloride in hydrochloric acid (1:1) (for reducing Fe^{III}), 0.2 ml of concentrated H_2SO_4, and 6 ml of a saturated solution of ammonium thiocyanate in acetone, and the volume made up to 10 ml with water; the optical density of the final solution was measured after a few minutes.

*A brief report of the material given in this article was given by P. N. Palei at the International Conference on the Peaceful Uses of Atomic Energy in Geneva in 1955, Reports of the Soviet Delegation at the International Conference on the Peaceful Uses of Atomic Energy "Research in the Fields of Geology, Chemistry, and Metallurgy," Acad. Sci. USSR Press, Moscow-Leningrad, 1955, p. 21.

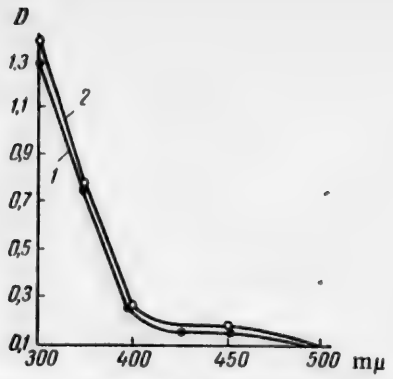

Fig. 1. Absorption curves for the uranium thiocyanate complex in an aqueous acetone medium (60% acetone by volume) (Curve 1), and in a mixture of methyl ethyl ketone and acetone (60% acetone by volume) (Curve 2). Uranium concentration 2.1 × 10^{-4} M.

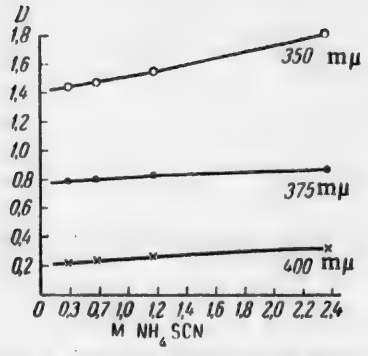

Fig. 2. Relation between the optical density of solutions of the uranium thiocyanate complex in methyl ethyl ketone–acetone mixtures (60% acetone) and thiocyanate concentration. Uranium concentration 2.1 × 10^{-4} M.

We found that small amounts of iron and copper (molar ratios of Fe and Cu to U of the order of 5 and 20 respectively) do not affect the optical density of the uranium thiocyanate complex in an aqueous acetone solution, when the measurements are made at 350 mμ. At a molar ratio of copper to uranium of 35, the optical density of the solution cannot be determined. Aluminum does not interfere with uranium determination even for large amounts of the former (Al_{mol}/U_{mol}) = 180) whatever wavelength is chosen for measuring the optical density of the solution of the uranium thiocyanate complex. The effect of small amounts of lead, cobalt, niobium, and molybdenum has already been noted in the literature [16].

Accordingly, the aqueous acetone medium can be used for the accurate quantitative spectrophotometric determination of uranium as its thiocyanate complex only after removing the uranium from a number of elements. In Fig. 1 (Curve 2) is shown the absorption of the uranium thiocyanate complex (uranium concentration 2.1 × 10^{-4} M) in a mixture of methyl ethyl ketone and acetone after quantitative extraction of uranium as its nitrate. This curve is similar to the absorption curve for the uranium thiocyanate complex in the aqueous acetone medium. The molar absorption coefficients(ϵ) of the uranium thiocyanate complex in the mixture of these solvents are somewhat greater than in the aqueous acetone medium and are equal to 6640, 3700, 1350, at 350, 375 and 400 mμ respectively.

The thiocyanate concentration has some effect on the light absorption of the uranium thiocyanate complex, particularly at 350 mμ (Fig. 2). This is connected, presumably, as in the case of aqueous solution, with a decrease in the dissociation of the uranium thiocyanate complex in the presence of large amounts of thiocyanate [17].

The color of the uranium thiocyanate complex develops rapidly, and the optical density is almost independent of the time for which the solution is allowed to stand, if the measurements are made at 375 and 400 mμ, while it increases at 350 mμ after being allowed to stand for 40 minutes (Fig. 3).

For the uranium concentrations examined (4.2 × 10^{-5} - 6.3 × 10^{-4} M) the solutions conform to the Bouger-Beer law for all the wavelengths* indicated (Fig. 4).

A study was made of the effect on the light absorption of the uranium thiocyanate complex of those elements, which either give colored compounds with thiocyanate (Fe, Cu, Co, Bi, Ti, and Mo) or possess an intrinsic color (e.g., V). Solutions of salts of these elements were added before the extraction to a saturated solution of ammonium nitrate containing uranyl nitrate.

*A few crystals of ascorbic acid were added to these solutions.

TABLE 1

Spectrophotometric Determination of Uranium as its Thiocyanate Complex, after Extraction with Methyl Ethyl Ketone from Solutions Containing Other Elements and Masking Agents (the amount of uranium taken in each case was 0.50 mg *)

Element added	Molar ratio of element to uranium	Optical density for the following wave length in mμ			Uranium obtained in mg at the following wavelength in mμ			Relative error in % at the following wavelength in mμ			Notes
		350	375	400	350	375	400	350	375	400	
U	—	1,40	0,78	0,27	—	—	—	—	—	—	Ascorbic acid added
U+Fe	43	1,40	0,78	0,27	0,50	0,50	0,50	0	0	0	The same
U+Fe	860	1,40	0,78	0,27	0,50	0,50	0,50	0	0	0	» »
U+Cu	38	1,40	0,77	0,28	0,50	0,495	0,505	0	−1,0	+1,0	» »
U+Cu	380	1,47	0,80	0,28	0,52	0,52	0,505	+4,0	+4,0	+1,0	» »
U+Co	40	1,40	0,79	0,28	0,50	0,505	0,505	0	+1,0	+1,0	» »
U+Co	400	1,42	0,79	0,28	0,505	0,505	0,505	+1,0	+1,0	+1,0	» »
U	—	1,40	0,62	0,20	—	—	—	—	—	—	Lactic acid added
U+Mo	25	1,38	0,61	0,20	0,49	0,49	0,50	−2,0	−2,0	0	The same
U+Zr	52	—	0,935	0,31	—	—	—	—	—	—	Zirconium nitrate added
U+Zr+V	Zr/U=52 V/U=50	—	0,927	0,315	—	0,497	0,503	—	−0,6	+0,6	The same
U+Zr+V+Fe+Cu+Co	Zr/U=52; V/U=50 Fe/U=43; Cu/U=38 Co U=40		0,925	0,315	—	0,495	0,503	—	−1,0	+0,6	» »
U+Mo+V+Fe+Cu+Co	Mo/U=25; V/U=50 Fe/U=43; Cu/U=38 Co/U=40		0,93	0,32	—	0,498	0,505	—	−0,4	+1,0	With re-extraction and subsequent addition of zirconium nitrate

*Each figure is the mean of five determinations.

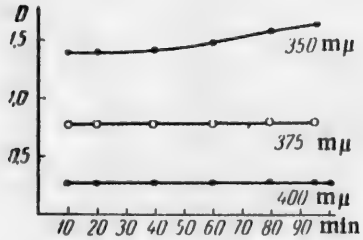

Fig. 3. Relation between the optical density of solutions of the uranium thiocyanate complex in mixtures of methyl ethyl ketone and acetone (60% acetone), and the time interval between formation of the complex and measurement of the density. Uranium concentration 2.1×10^{-4} M.

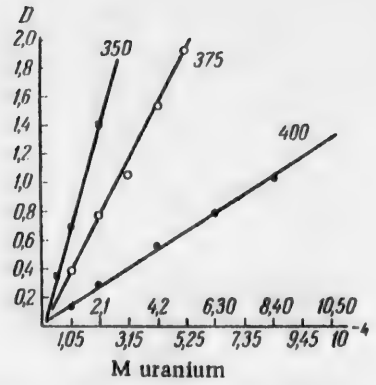

Fig. 4. Relation between the optical density of solutions of the uranium thiocyanate complex in methyl ethyl ketone–acetone mixtures (60% acetone) and uranium concentration.

As the experiments showed, the presence of Fe^{III}, Cu^{II}, Bi, Tl^{IV} in the solution prior to extraction, led to an increase in the optical density of the uranium thiocyanate complex in the organic layer; this indicates partial extraction of these elements by methyl ethyl ketone. Molybdenum depresses the optical density of the uranium thiocyanate complex in the same way as it does in an aqueous acetone medium. Apparently, molybdate ions partially complex uranium as a poly compound.

For suppressing the effect of small amounts of Fe^{III}, Cu^{II}, and Co^{II} extracted by the methyl ethyl ketone, it proved sufficient, as experiments showed, to add a few crystals of ascorbic acid to the uranium thiocyanate complex in the methyl ethyl ketone–acetone mixture. When this technique is adopted the optical density of the uranium thiocyanate complex does not change (Table 1). We tried to eliminate interference on the part of V^{V} and Mo^{VI} by modifying the extraction conditions (adding reducing agents to the solution: $SnCl_2$, ascorbic acid, hydrazine sulfate; changing the pH; and adding Complexones I and III as masking agents [18]). Nevertheless, there was observed in all cases, either low (in the presence of Mo) or high (in the presence of V) values of the optical density of the uranium thiocyanate complex in the organic layer. It is of interest to note that in the presence of Complexon I, uranium is incompletely extracted by methyl ethyl ketone, while in the presence of Complexon III it is not extracted at all, although it is known that uranium forms compounds which have a low stability with these complexons [19]; we also confirmed this fact by a polarographic method. We established that by complexing the molybdenum, prior to extraction, as its complex with lactic acid*, its effect on the extraction of uranium with methyl ethylketone and on the subsequent measurement of the optical density of the uranium thiocyanate complex, could be completely eliminated (Table 1). Nevertheless, when such a technique is used, there is some decrease in the optical density of the uranium thiocyanate complex at 375 and 400 mμ (Table 1). Accordingly, in order to prepare calibration curves, it is necessary prior to extraction to add 1 ml of a 40% solution of lactic acid to the solution to be extracted.

The effect of vanadium cannot be removed by addition of lactic acid; V^{V} is reduced by lactic acid to V^{IV} or V^{III} (depending on temperature and duration of reduction), which absorb appreciably at 350-400 mμ [15]. Accordingly, zirconium nitrate** was added to the solution to be extracted in order to complex the vanadium. When this technique is used, although the optical density of the uranium thiocyanate complex in the organic layer thereby increases, (this indicates partial extraction of zirconium nitrate by the methyl ethyl ketone), the optical density nevertheless remains constant whatever the amount of vanadium in the solution being extracted. Accordingly,

*To 9 ml of a saturated solution of ammonium nitrate containing uranyl nitrate and ammonium molybdate, was added 1 ml of a 40% solution of lactic acid.

**1 ml of a 4.7% solution of $Zr(NO_3)_4 \cdot 5H_2O$ was added to 9 ml of solution.

TABLE 2

Determination of Uranium in Ores*

Sample No.	By the spectrophotometric method in %, at mμ:		By a volumetric method, %	Difference in %, at mμ:	
	375	400		375	400
1	0,105	0,108	0,105	—	+0,003
2	0,91	0,87	0,87	+0,04	—
3	0,285	0,285	0,288	—0,003	—0,003
4	0,325	0,330	0,325	—	+0,005
5**	0,090	0,090	0,085	+0,005	+0,005
6	0,270	0,270	0,270	—	—

*Each figure is the mean of six determinations; the deviation of individual results from the mean does not exceed ± 3%.

**Weight ratio of V:U = 10:1.

for the analysis of materials containing uranium and vanadium (and also Fe, Cu, and Co) it is necessary to construct calibration curves by adding to the standard solutions which are to be extracted, 1 ml of a 4.7% solution of zirconium nitrate; the light absorption of the uranium thiocyanate complex should be measured at 375 and 400 mμ when zirconium is present, since at 350 mμ zirconium interferes strongly.

When both molybdenum and vanadium are present in the test material (as well as Fe, Cu, and Co) it is not enough merely to extract the uranyl nitrate with methyl ethyl ketone, since the simultaneous addition of lactic acid (in order to complex the molybdenum), and zirconium nitrate (to complex the vanadium) to the test solution, leads to the formation of a bulky colloidal precipitate of zirconium lactate. In such cases satisfactory results can be obtained by using an intermediate re-extraction of the uranium with ammonium carbonate solution. First of all, the uranium is extracted with methyl ethyl ketone from a saturated solution of ammonium nitrate to which has been added 1 ml of a 40% solution of lactic acid (per 10 ml). Uranium is then re-extracted from the organic layer by a three fold treatment with 3 ml of 2% ammonium carbonate solution. The carbonate solution is evaporated to dryness and the residue calcined in a muffle at 500-600°* for 10-15 minutes; on cooling, the residue is dissolved in 2-3 ml of HNO_3(sp. gr. 1.39). The solution is evaporated to dryness and the residue dissolved in 9 ml of a saturated solution of ammonium nitrate, 1 ml of a 4.7% solution of zirconium nitrate is added and the uranium extracted twice with 2 ml lots of methyl ethyl ketone; the extracts are collected in a 10 ml standard flask, 6 ml of a saturated solution of ammonium thiocyanate in acetone is added, and the volume made up to the mark with methyl ethyl ketone. Ascorbic acid should not be added in this case, since it enhances the light absorption of the uranium thiocyanate complex in the final solution should the test material contain molybdenum and vanadium.

Calibration curves should be constructed by measuring the light absorption of standard solutions prepared in exactly the same way.

As a result of the work carried out, several variants of the method can be suggested which are based on extraction of the uranium with methyl ethyl ketone, with subsequent spectrophotometric determination of the uranium as its thiocyanate complex.

The first variant is applicable in the absence of Mo, V, Ti, and Bi, and in the presence of iron, copper, cobalt, and other elements in the test material. Uranium is extracted as uranyl nitrate from a solution, which is saturated with respect to ammonium nitrate, by means of methyl ethyl ketone; the thiocyanate complex of uranium** is obtained in the ketone phase, and the optical density of the solution is measured after addition of a few crystals of ascorbic acid (for eliminating the effect of traces of Fe^{III}, Cu^{II}, and Co^{II}).

*When calcining is omitted high results are obtained.

**Analytical grade ammonium thiocyanate should be used, and material taken from the same supply or bottle should be used for the analysis and for constructing the calibration curves.

It takes 20-30 minutes to carry out an analysis by this variant, without taking into account the time taken to get the material into solution. The experimental accuracy is 1-2% relative.

The second variant is applicable in the presence of Mo, Fe, Co, Cu, and other elements, but in the absence of V and Ti, and differs from the first variant only in that, prior to extraction, 1 ml of 40% lactic acid solution is added to the test solution in order to complex the molybdenum. The time taken to carry out an analysis and the accuracy are the same as for the first variant.

The third variant is applicable in the presence of V, Fe, Co, Cu, and other elements, but in the absence of Mo, and differs from the first and second variants only in that, prior to extraction, 1 ml of a 4.7% solution of zirconium nitrate is added to the solution to complex vanadium.

The fourth variant is applicable when the sample contains Fe, Cu, Co, V, Mo and other elements and differs from all the other variants, in that an intermediate stage of reextraction of the uranium is used. From the methyl ethyl ketone layer, after the first extraction, (in the presence of lactic acid) the uranium is reextracted three times by means of a 2% solution of ammonium carbonate (5 ml each time); the solution is evaporated to dryness, and the residue calcined in a muffle, it is then dissolved in HNO_3, the solution is saturated with ammonium nitrate and zirconium nitrate solution is added, the uranium is then extracted again with ketone. A solution of ammonium thiocyanate in acetone is added to the methyl ethyl ketone phase and the light absorption measured. This variant of the method takes 3-4 hours. The accuracy is 1.5-2% relative.

Table 2 contains results of determinations of uranium in six samples of ore in which the content of this element had been established by chemical methods. The first five samples were analyzed by the third variant, while sample six was analyzed by the fourth variant. The method gives satisfactory results.

SUMMARY

Conditions have been established for the spectrophotometric determination of uranium in the form of its thiocyanate complex (after extraction of uranium as uranyl nitrate by means of methyl ketone) in samples which contain Fe, Cu, Co, V, Mo, and other elements.

The spectrophotometric method permits determination of 0.01-1.0% of uranium in ores (and other materials). The relative error is ± 2-3%.

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DETERMINATION OF URANIUM BY THE FLUORIDE METHOD WITH A FINAL TITRIMETRIC DETERMINATION*

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In 1948, while studying the phenomena which occur in solutions containing hydrofluoric acid, divalent iron, and salts of sexivalent uranium, we became aware that divalent iron is capable, under these conditions, of quantitatively reducing uranium to the quadrivalent state. In acid media, in the absence of fluoride ions, trivalent iron oxidizes quadrivalent uranium:

$$UO^{2+} + 2Fe^{3+} + H_2O \rightarrow UO_2^{2+} + 2Fe^{2+} + 2H^+. \quad (1)$$

Auger's method [1], for example, which was checked and confirmed recently by Weiss and Blum [2], is based on this reaction. Trivalent iron is added as a catalyst to the solution of quadrivalent uranium during its titration with dichromate [3].

Depending on the hydrofluoric acid concentration, the oxidation–reduction potentials of the system U^{VI}/U^{IV} and Fe^{III}/Fe^{II} changes, the potential of the system U^{VI}/U^{IV} increases strongly, while the potential of the system Fe^{III}/Fe^{II} drops appreciably (Fig. 1); at the point where the hydrofluoric acid concentration is 2-3 moles/liter, the potential of the system Fe^{III}/Fe^{II} becomes 0.17-0.20 volt more electronegative than the potential of the system U^{VI}/U^{IV}. In practice, such a potential difference is sufficient to ensure that the following reaction can proceed:

$$UO_2^{2+} + 2Fe^{2+} + 4H^+ + 16F^- \rightarrow UF_4 + 2[FeF_6]^{3-} + 2H_2O \quad (2)$$

According to our results, the latter reaction occurs within a very wide range of hydrogen ion concentration, starting at a pH of 4-5.

On the basis of this principle we have developed two rapid methods for the determination of uranium [5]. One of them which was designed for the determination of small amounts of uranium with a photometric finish was published recently [6], the other, with a titrimetric finish is described below.

Some of the Properties of the Simple and Double Fluorides of Quadrivalent Uranium

Despite a widely held opinion [7], the fluoride of quadrivalent uranium is appreciably soluble in hydrofluoric acid [8] and cannot be used for the quantitative determination of uranium. As long ago as 1936, Khlopin and Gerling [9] came to the conclusion that the double fluoride of quadrivalent uranium and ammonium is considerably less soluble than the simple fluoride of uranium, and suggested precipitating quadrivalent uranium in an acetate buffer medium in the presence of excess ammonium fluoride.

However, according to our results (1949), of the double compounds of uranium (IV) fluoride with the alkali metals**, only the double fluoride of uranium (IV) and sodium has a sufficiently low solubility and is precipitated

*This work was carried out in 1948-1952.

** The following double fluorides were examined: uranium(IV)-sodium, uranium (VI)-calcium, uranium (IV)-ammonium, and uranium (IV)-lithium.

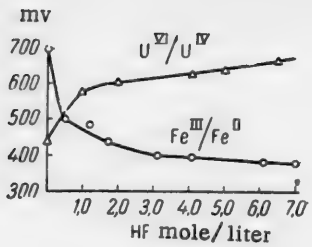

Fig. 1. The actual potential of the systems U^{VI}/U^{IV} and Fe^{III}/Fe^{II} as a function of the hydrofluoric acid concentration in 1 N sulfuric acid.

almost completely, not only in an acetate buffer, but also in a mineral acid medium. Its solubility in an n-molar solution of hydrofluoric acid (n = 1, 2, 3, 4) containing sulfuric acid at concentrations from 0.01 to 1 N, and from 2 to 10% sodium sulfate, amounts to 0.1-0.15 mg of U in 100 ml. In the presence of excess sodium salts, e.g., at U:Na = about 1:10 and 1:40, in solutions of hydrofluoric acid containing sulfuric acid, the same anhydrous compound $NaUF_5$ is always formed. It crystallizes in the hexagonal crystal system, but with different parameters for the elementary cell:

$$a = 4{,}47 \pm 0{,}05\text{A}, \quad c = 7{,}24 \pm 0{,}05\text{A} \text{ and } a = 4{,}17 \pm 0{,}05\text{A}, \quad c = 6{,}76 \pm 0{,}05\text{A}.$$

The difference between the completeness of precipitation of simple uranium (IV) fluoride and its double fluoride $NaUF_5$ can be illustrated by the determination of uranium (IV) in a sample of synthetic pitchblende (sample 466). The determination was carried out twice; first, the fluoride was isolated by a generally accepted procedure [7], i.e., from a solution containing 5-10 ml of hydrofluoric acid in 100 ml of solution, the second time it was isolated by the same procedure, but with the modification that during the treatment of an aliquot with hydrofluoric acid in a platinum basin, 2 g of sodium sulfate was added. The difference between the results was very great: When no sodium sulfate was used 3.88% U was found, while when sodium sulfate was used the amounts found were 27.48 and 27.02% U.

The experimental results (Table 1) clearly demonstrate the very close relation between completeness of precipitation of the double fluorides of uranium (IV) and the nature of the cation. The fluorides were isolated after reduction of uranium with divalent iron under the following conditions: in experiments 1-6, 5.0-5.5 ml of sulfuric acid 1:1, 2 g of Mohr's salt, 10 ml of 40% hydrofluoric acid, and 2 g of sodium sulfate were added to a known volume of a weakly acid standard solution of uranyl sulfate, the final solution was diluted with water to 100 ml; the sulfuric acid concentration thereupon is lowered to about 1 N. The whole was thoroughly mixed and the precipitate allowed to stand overnight. The precipitate was filtered off and washed with wash liquor with a pH of about 2(50 ml of hydrofluoric acid + 40 g of ammonium acetate, and the volume made up to 1 liter with water) until the washings gave a negative reaction for divalent iron (test with orthophenanthroline or α,α'-dipyridyl). The residue was then titrated with 0.01 N vanadate solution using phenanthranilic acid as indicator.

In experiments 7-15, in order to simulate the conditions used by Khlopin and Gerlin [9], acetate was added instead of sulfuric acid until the pH was 1.6-2.0. In experiments 7-11, 4 g of sodium acetate was added in each case, while in experiments 12-15, in order to compare the effect of the cation, 5 g of ammonium acetate was added.

Experiments showed that even in an acetate medium, i.e., under those conditions indicated by Khlopin and Gerling [9], positive results are only obtained in the presence of sodium salts (compare experiments 7-11 with experiments 12-15). In addition to this, in experiments 1-6 in 1 N sulfuric acid, despite the presence of sodium salts, there is observed a systematic drop in the results on the average equal to 0.32 mg of uranium.

On this basis it would appear that in order to obtain complete precipitation of the double fluoride of uranium (IV) and sodium, the acetate buffer mixture is to be preferred. Nevertheless, it was found that the buffered medium is only suitable for the determination of uranium in pure solutions (e.g., in an uranium pitchblende), since at a relatively high pH, in addition to uranium there are precipitated the compounds of trivalent and divalent iron, quadri- and trivalent vanadium, calcium and magnesium fluorides, etc., as a result of which washing of the precipitate and the oxidimetric titration of uranium becomes impossible.

Thus, in order to determine uranium in mineral raw material by the fluoride method, we decided to use precipitation of the double fluoride $NaUF_5$ from a mineral acid medium, and apply some empirical corrections.

TABLE 1

Precipitation of Uranium (IV) in the Form of its Double Fluorides with Ammonium and Sodium in an Acetate or Mineral Acid Medium in the Presence of Hydrofluoric Acid

Test No.	0.01 N solution of U taken, ml	0.01 N NH_4VO_3 used, ml	Deviation			Added		
			0.01 N solution, ml	U, mg	in relative %	sodium acetate	ammonium acetate	sodium sulfate
1	22,13	21,86	−0,27	−0,33	− 1,3	—	—	2
2	22,13	21,79	−0,34	−0,40	− 1,5	—	—	2
3	22,13	21,87	−0,26	−0,30	− 1,2	—	—	2
4	17,44	17,22	−0,22	−0,26	− 1,2	—	—	2
5	17,44	17,20	−0,24	−0,28	− 1,3	—	—	2
6	17,44	17,15	−0,29	−0,34	− 1,6	—	—	—
Mean			−0,27	−0,32	− 1,3			
7	12,69	12,67	−0,02	−0,02	− 0,1	4	—	—
8	12,69	12,64	−0,05	−0,06	− 0,4	4	—	—
9	12,69	12,64	−0,05	−0,06	− 0,4	4	—	—
10	12,69	12,67	−0,02	−0,02	− 0,1	4	—	—
11	12,69	12,69	±0,00	±0,00	± 0,0	4	—	—
None			−0,03	−0,03	− 0,2			
12	22,13	16,07	−6,06	−7,21	−27,7	—	5	None
13	22,13	17,30	−4,83	−5,75	−22,1	—	5	—
14	22,13	17,48	−4,65	−5,53	−21,2	—	5	—
15	22,13	17,82	−4,31	−5,13	−19,7	—	5	—
Mean			−4,96	−5,90	−22,7			

The Effect of Foreign Ions on the Determination of Uranium as the Double Fluoride of Uranium (IV) and Sodium in a Mineral Acid Medium

Uranium often turns up in ores and rocks. For its determination in mineral raw material, primary attention must be given to the behavior of vanadium.

The normal oxidation−reduction potentials of the systems U^{VI}/U^{IV} and V^{IV}/V^{III} are very close; the potential of U^{VI}/U^{IV} is equal to 0.407± 0.003 volt [10], while the potential of V^{IV}/V^{III} is equal to 0.337 volt [11]. Accordingly, it is almost impossible, in practice, to choose a reducing agent, which, while quantitatively reducing uranium to the quadrivalent state, does not, at the same time, reduce vanadium to the trivalent state, even if only partially. In an acid medium, divalent iron reduces quinquevalent vanadium to the quadrivalent state. But, in an acid medium in the presence of hydrofluoric acid, iron (II) reduces vanadium to the trivalent state in connection with the formation of a stable fluoride complex of trivalent vanadium, while the potential of the system V^{IV}/V^{III} increases so much that it becomes more electropositive than the potential of the system Fe^{III}/Fe^{II} (Fig. 2).

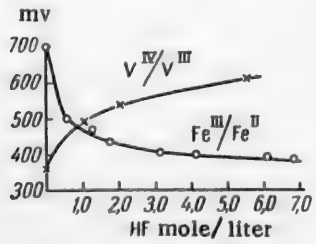

Fig. 2. The actual potential of the system Fe^{III}/Fe^{II} and V^{IV}/V^{III} in 1 N sulfuric acid as a function of hydrofluoric acid concentration.

The analogy between uranium and vanadium can be taken even further, namely the capacity of the tri- and quadrivalent compounds of vanadium to form double fluorides with the alkali metals [12], while, as we established, in certain cases, these fluorides are not completely soluble in an acid medium and can contaminate the precipitate of quadrivalent uranium.

During oxidimetric titration with vanadate, contamination of the uranium precipitate with trivalent vanadium cannot be allowed, since it is oxidized by the vanadate to the quadrivalent state: $(V^{III} + V^{V} \rightarrow 2V^{IV})$.

A solution was found in the difference in solubility of the double fluorides of vanadium (III) and uranium (IV); the

TABLE 2

Determination of Uranium in the Presence of Vanadium (20 mg), Molybdenum (15 mg), and Titanium (15 mg) by Reduction with Divalent Iron in 1 N Sulfuric Acid, Containing 2% Sodium Sulfate and 10% (by Volume) of Hydrofluoric Acid

0.01 N U solution taken, ml	0.01 N NH_4VO_3 used, ml	Deviation		U found in the filtrate, mg
		0.01 N solution, ml	U mg	
8,72	8,38	—0,34	—0,40	0,11
8,72	8,47	—0,25	—0,29	0,11
9,13	8,86	—0,27	—0,32	0,09
9,13	8,81	—0,32	—0,38	0,11
22,89	22,50	—0,39	—0,46	0,13
22,89	22,60	—0,29	—0,34	0,15
22,89	22,50	—0,39	—0,46	0,12
				0,12
	Mean	—0,32	—0,37	

TABLE 3

Determination of Uranium in the Presence of Iron (350 mg), Vanadium (20 mg), Molybdenum (15 mg), and Titanium (15 mg) by Reduction with Divalent Iron in 1 N Sulfuric Acid, Containing 2% Sodium Sulfate and 10% (by Volume) of Hydrofluoric Acid

0.01 N U solution taken, ml	0.01 N NH_4VO_3 used, ml	Deviation	
		0.01 N NH_4VO_3 used, ml	U, mg
7,57	7,35	—0,22	—0,26
7,57	7,23	—0,34	—0,40
7,57	7,31	—0,26	—0,31
12,70	12,52	—0,18	—0,21
12,70	12,34	—0,36	—0,42
12,70	12,39	—0,31	—0,36
12,70	12,42	—0,28	—0,33
12,70	12,44	—0,26	—0,30
12,70	12,52	—0,18	—0,21
12,70	12,42	—0,28	—0,33
	Mean	—0,27	—0,31

fluoride Na_2VF_5 is considerably more soluble and remains in solution in 1 N sulfuric acid, while the fluoride $NaUF_5$ is precipitated quantitatively. For this purpose, it is essential that the concentration of the sodium salt should not exceed 2%.

The effect of other foreign elements was eliminated, mainly in two ways. Some of these elements are removed from the sphere of reaction in that they stay in solution during precipitation of uranium (IV) fluoride, these elements include, e.g., niobium, tantalum, molybdenum*, titanium, and other elements whose fluorides

*Under the conditions used for reducing uranium, molybdenum is reduced to molybdenum blue which remains in solution as a colloidal suspension, so that, in practice, it is possible to remove it almost completely by washing it off the precipitate.

TABLE 4

Comparative Results for the Determination of Uranium by the Fluoride and the Hydrosulfite Method [5] in Control Samples

Sample No.	Impurities in the aliquot, in mg				U found (%) by the following methods:		Deviation, relative, %
	Fe^{III}	V^{V}	Mo^{VI}	Ti^{IV}	fluoride	hydrosulfite	
1	None	None	None	None	53,17	52,80	+0,7
1	—	—	—	—	52,83	—	+0,0
1	—	—	—	—	53,31	—	+1,0
1	350	20	15	15	53,37	—	+1,1
1	350	20	15	15	53,22	—	+0,9
1	350	20	15	15	53,11	—	+0,6
1	350	20	15	15	53,11	—	+0,6
P-X	None	None	None	None	15,37	14,94	+2,8
P-X	»	»	»	»	15,22	—	+1,9
P-X	350	20	15	15	15,23	—	+1,9
P-X	350	20	15	15	15,26	—	+2,1
Cl-X	None	None	None	None	10,56	10,45	+1,0
Cl-X	»	»	»	»	10,61	—	+1,4
Cl-X	350	20	15	15	10,60	—	+1,4
Cl-X	350	20	15	15	10,59	—	+1,3
VII-b	None	None	None	None	3,06	3,13	−2,2
VII-b	»	»	»	»	3,14	—	+0,3
VII-b	»	20	15	15	3,12	—	−0,3
VII-b	»	20	15	15	3,12	—	−0,3

are soluble in an acid medium. Another part of the elements is precipitated partially with uranium fluoride (IV), but do not interfere further during the oxidimetric determination of uranium, these elements include, e.g., iron (III)*, aluminum**, calcium **, and the rare earths**.

Tables 2 and 3 contain results for the determination of uranium in synthetic mixtures, containing appreciable amounts of trivalent iron, vanadium, molybdenum, and titanium.

As already indicated above, all the results are characterized by a deviation of 0.3-0.35 mg of uranium on the low side. This deviation is composed of two factors: the solubility of $NaUF_5$ during its precipitation in 1 N sulfuric acid, and during washing of the precipitate. These losses were compensated by a) using an empirical titer for the vanadate, the latter was established by using a standard solution of sexivalent uranium, and titrating the precipitate of $NaUF_5$ which was isolated and washed under the conditions used in the experimental procedure, or b) by applying a correction of 0.30-0.35 mg of U. Table 4 contains comparative results for the determination of uranium by two methods in two samples with different uranium contents, and also containing iron, vanadium, molybdenum, and titanium.

Experimental Procedure for the Determination of 3-60% of Uranium in the Presence of Iron, Vanadium, Molybdenum, and Titanium

Depending on the expected content of uranium, an aliquot of 0.2 to 1 g of sample is decomposed as usual by boiling in a mixture of nitric acid (sp. gr. 1.4) and hydrochloric acid (sp. gr. 1.19) and excess acid removed by evaporation. To the residue is added 23-25 ml of sulfuric acid and the mixture heated to the appearance of

*Before titration with vanadate, the washed precipitate of the fluorides is treated with sulfuric acid in the presence of boric acid, during which the double fluoride of trivalent iron $Na_3[FeF_6]$ is decomposed, and the iron (III) oxidizes the uranium to form the equivalent amount of ferrous iron which is then oxidized by vanadate.

**Appreciable amounts of calcium, aluminum, and the rare earths may exhibit interference. The method of removing such interference is described in the experimental procedure.

thick white fumes. 50-60 ml of water is added and the whole boiled for 20-30 minutes to dissolve the salts. Solution plus precipitate is transferred to a 200 ml standard flask. The solution obtained contains approximately 2 N sulfuric acid.

In order to determine uranium, 25.00-50.00 ml* of this solution is pipetted into a platinum basin or a paraffin beaker** and the necessary reagents added in such amounts that the final volume of 100 ml contains the following: 1 N sulfuric acid, 2% Mohr's salt, 2% anhydrous sulfate, and 10% (by volume) of 40-48% hydrofluoric acid. The solution is thoroughly mixed until the salts have completely dissolved and then it is left to stand for 5 hours or overnight. The precipitate is filtered through a paraffined funnel using a fine filter paper (blue band), and the filtrate collected in a paraffined beaker. The precipitate is transferred onto the filter paper and washed with wash liquor with a pH of about 2 (50 ml of hydrofluoric acid + 40 g ammonium acetate + distilled water to 1 liter) until the wash liquors give a negative reaction for divalent iron (test with 5-orthophenanthroline, α,α'-dipyridyl*** or permanganate).

Depending on the expected concentration of uranium, the determination is completed by titration with 0.01 or 0.005 N ammonium vanadate. For this purpose, the washed precipitate together with the filter paper are transferred to a 250-300 ml conical flask which contains 90 ml of a 33% by volume acid, 10 ml of saturated solution of boric acid, and 2-3 drops of a 0.1% solution of phenylanthranilic acid. The solution is thoroughly mixed and then titrated with vanadate to the appearance of a rosy violet color which becomes more intense with time.

Determination of uranium in 10-12 samples takes 10-12 hours, not taking into account the time for which the precipitate is allowed to stand.

SUMMARY

A titrimetric method has been developed for the determination of uranium in the presence of iron, vanadium, molybdenum, and titanium; it is based on the fact that divalent iron in sulfuric acid, in the presence of hydrofluoric acid, reduces uranium (VI), and the quadrivalent uranium is precipitated in the form of the double fluoride $NaUF_5$; the uranium determination is finished vanadometrically.

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*The aliquot chosen should be such that 10-20 ml of a 0.01 or 0.005 N solution of oxidizing agent is used for titration. In the presence of large amounts of calcium, or the rare earths, care should be taken that the aliquot does not contain more than 25-30 mg of Al_2O_3, or more than 20-25 mg of calcium or total rare earths, since large precipitates complicate washing somewhat, and can lead to high results at the expense of divalent iron.

**Since plexiglass apparatus is not readily available at the moment, and the analysis is carried out at room temperature after decomposing the sample, vessels which have been covered with paraffin can be used (200-300 ml beakers, funnels). The vessels are recoated with paraffin as the need arises.

***Orthophenanthroline or α,α'- dipyridyl are used as follows for testing that the precipitate has been washed completely: the funnel is filled with wash liquor which is then collected in a platinum basin, a few crystals of α,α'-dipyridyl or phenanthroline are added to the basin and the crystals and liquid mixed by swirling the basin. In the absence of ferrous ions the solution remains colorless; when ferrous ions are present the solution acquires a rose color.

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QUANTITATIVE DETERMINATION OF OXYGEN IN THE LOWER OXIDES OF TITANIUM BY MEANS OF X-RAY ANALYSIS

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Under the conditions of gradual oxidation of titanium, solid solutions are formed by the penetration of oxygen atoms into the octahedral cavities of the crystal lattice of α-Ti. According to Ehrlich [1] solid solutions of oxygen in α-titanium are formed up to the composition $TiO_{0.42}$. All the phases with a variable composition $Ti_{0\rightarrow0.42}$ can be called the lower oxides of titanium. The conditions for the formation of the lower oxides of titanium, and also of its other oxides with a higher oxygen content are being studied fairly thoroughly at present. The equilibrium phase diagram for the system titanium–oxygen [2] is known.

Radiographical studies of the lower oxides of titanium [1, 2] have shown that the curve relating the lattice constant c and the oxygen content of the α-titanium, which possesses a hexagonal crystal lattice, is steep. This makes it possible to attempt to use a radiographic method for the quantitative determination of oxygen dissolved in α-titanium. Such an attempt was made in the work described here.

Synthesis of the Preparations of the Lower Oxides of Titanium. In order to check on, and get more accurate values than the published ones, we prepared and examined radiographically some preparations of the lower oxides of titanium TiO_x from $TiO_{0.05}$ to $TiO_{0.60}$ through $x = 0.05$. Titanium iodide in the form of small bars was used as the original material. The purity of the titanium was 99.8%, while the impurities present and their amounts were 0.05% Si, 0.05% Mg, 0.03% Fe, 0.01% Cu and 0.06% others.

In contrast to previous workers [1, 2] who prepared the lower oxides of titanium by sintering titanium metal with TiO_2, we synthesized preparations by saturating powdered titanium with gaseous oxygen. Titanium in the form of a fine powder which readily reacts with gaseous oxygen, was prepared by the hydride method. The oxygen and hydrogen contents of the titanium power thus prepared were determined by a vacuum extraction method [3]. Analysis showed that the oxygen concentration was 0.04% by weight, while the hydrogen content was 0.003% by weight.

A quartz boat filled with titanium powder (about 1.5 g) was placed in a quartz tube and the air pumped out of the system; the temperature was gradually taken up to 350° until all the gases and traces of moisture adsorbed by the powder had been removed by continuous operation of an oil diffusion pump. The calculated amount of oxygen, obtained by the electrolysis of water, was then allowed into the cooled system. The oxygen pressure in a known volume was measured by a mercury U-shaped manometer. In the temperature range 500-550° complete absorption of the oxygen by titanium was observed. The amount of absorbed oxygen was also determined from the gain in weight of the sample. Preparations of the titanium oxides obtained in the form of powders were pressed in columns into the form of cylinders at a pressure of about 8000 kilogram/cm^2, and kept for 15 hours at a temperature of $1000 \pm 20°$ in a quartz tube in order to achieve a uniform distribution of oxygen in the preparation.

Weighing of the calcined samples of the oxides from $Ti_{0.05}$ and $Ti_{0.30}$ showed that their weight decreased by 0.4-0.7 thousandths part of a gram as the result of the evaporation of the lower oxides of titanium, since a small bluish film was observed on the inner walls of the tube [1].

The preparations of the lower oxides of titanium obtained, on fracture, have a light grey color, and on being triturated become dark.

Samples of $TiO_{0.20}$ and $TiO_{0.40}$ were analyzed for oxygen and hydrogen by the vacuum fusion method [3]

Calculated O_2 content % wt.	O_2 found by the vacuum method, %
6.40	6.37
11.77	11.75

The calculated amount of oxygen absorbed by the sample was taken as a basis.

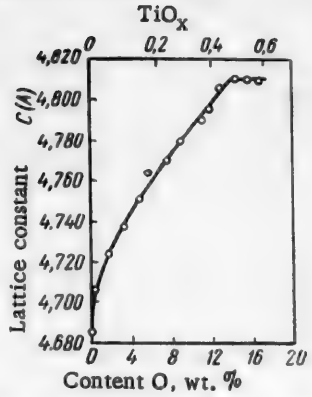
Radiographical Determination of Lattice Constants. The preparations of the lower oxides of titanium obtained, after being ground into a fine powder, were annealed in a vacuum at 500-600° for 30 minutes in order to relax the stress of the crystal lattice, they were then examined radiographically by the powder method (Debye-Scherrer). It was essential to get the most accurate values of the lattic constants of the test samples. This could be carried out either by using the x-ray method of "reciprocal photography" in a camera of type 1 KROS, or by the asymmetric method of Straumanis and Jevins [4]. We used the latter method since it ensures that clearer radiograms are obtained in the region of large scattering angles for shorter exposures than is possible when the method of "reciprocal photography" is used. The technical details of the asymmetric method for the precision determination of the lattice constants of the elementary cell of crystals have been described previously [5]. One of the most important conditions for ensuring the maximum accuracy of the method is the preparation of very fine powder samples, with a thickness of less than 0.2 mm, prepared by depositing on filaments of borlithium glass a fine layer of the test powder by means of non-drying flexible dope.

Composition and Values of the Lattice Constants for the Lower Oxides of Titanium

Chemical composition			a (A)	c (A)	c/a
TiO_x	O, at %	O, wt., %			
α-Ti	0	0	2,9510	4,6850	1,5875
$TiO_{0,012}$	1,19	0,40	2,9515	4,7054	1,5942
$TiO_{0,053}$	5,03	1,74	2,9556	4,7225	1,5978
$TiO_{0,102}$	9,27	3,30	2,9610	4,7370	1,5998
$TiO_{0,154}$	13,24	4,87	2,9640	4,7510	1,6029
$TiO_{0,193}$	16,20	6,05	2,9670	4,7616	1,6049
$TiO_{0,248}$	19,62	7,62	2,9695	4,7701	1,6064
$TiO_{0,299}$	22,95	9,06	2,9703	4,7789	1,6089
$TiO_{0,337}$	25,06	11,10	2,9702	4,7901	1,6127
$TiO_{0,401}$	26,55	11,77	2,9785	4,7950	1,6153
$TiO_{0,451}$	31,01	13,03	2,9705	4,7992	1,6156
$TiO_{0,513}$	33,87	14,60	2,9710	4,8105	1,6192
$TiO_{0,510}$	35,82	15,71	2,9704	4,8101	1,6193
$TiO_{0,600}$	37,53	16,68	2,9701	4,8097	1,6194

In order to remove the fluorescent background which develops during x-ray analysis of titanium-containing materials, we used a second x-ray plate placed between the sample and the main plate as a screen. The radiograms obtained in this way had a considerably weakened background, and contained all the weak lines; under these conditions, the K_α lines with large angles were clearly duplicated.

Radiograms were taken in ordinary cameras with a diameter of 57.3 with copper radiation, the operating conditions of the tube being 35 kilovolts and 14 milliamps. The exposure on an average was 12 hours. In order to calculate the lattice constants a and c, bright, readily duplicated lines with the indices (2133) and (3032), and having angles of the order of 69 and 73° respectively were chosen. The lines were measured on the radiograms in an IZA-2 comparator with an accuracy of ± 0.01-0.02 mm. The values of the lattice constants calculated from these two lines had an accuracy of ± 0.0004 A. A check on the value of the constant c, carried out for several samples on the basis of the line (0006) showed that the results agreed. We used the following



The relation between the lattice constant c and the oxygen content in the lower oxides of titanium: c = f (x).

values of the wavelengths for the calculations: $\lambda CuK\alpha_1$ = 1.54050 A and $\lambda CuK\alpha_2$ = 1.54434 A. The final values of the lattice constants were calculated as the arithmetic mean of four possible combinations for the lines: $2133\alpha_1$, $2133\alpha_2$, $3032\alpha_1$ and $30\overline{3}2\alpha_2$.

The composition of the preparations of the lower oxides of titanium which we studied and the values of their lattice constants are given in the table. Titanium oxide which we prepared and which contained 0.40% by wt. of oxygen, according to our analysis, was used as the preparation with a composition of $TiO_{0.012}$

Indexing of the radiograms showed that all the lines observed for samples ranging from the original titanium to an oxide with a composition of $TiO_{0.5}$ belong to the hexagonally closely packed structure α Ti. Starting with the oxide $TiO_{0.5}$ on the radiograms there appeared a system of weak lines corresponding to the phase on a variable composition based on TiO. Thus, it can be assumed that the homogeneity boundary of solid solutions of oxygen in α-Ti corresponds approximately to the composition $TiO_{0.48}$.

The Standard Curve c = f (x) for Determination of Oxygen. As is evident from the Table, the lattice constant c changes to a considerably greater extent than the constant a in the lower oxides of titanium, with increasing oxygen content. For solving our problem therefore we used the values of the constant c.

On the basis of the tabulated results, a curve was constructed relating the lattice constant c to the oxygen content of the lower oxides of titanium [i.e., the curve c = f(x)] The oxygen content in wt. % was plotted along the abscissa, as well as the values of the oxygen coefficient x in the formula TiO_x. This curve can be used as a standard for the quantitative determination of oxygen in the lower oxides of titanium belonging to the binary system titanium–oxygen. By maintaining the accuracy which we achieved for the determination of the lattice constant c, which is equal to ± 0.0004 A, the accuracy of determining oxygen by means of the curve c = f x) by the interpolation method amounts to ± 0.1% wt. of oxygen on an average. In the region of very low oxygen contents (at approximately up to 1% wt. of oxygen) the accuracy will be even higher. As is evident from the curve, the maximum solubility of oxygen in α-Ti corresponds approximately to 14.4% wt. In order to determine oxygen quantitatively in the lower oxides of titanium by the x-ray method, radiograms are taken of the test material in the form of a powder, the lattice constant c being measured with the maximum accuracy. The value found for c is plotted on the curve c = f (x) in the form of a circle with a radius with corresponding accuracy in A. The oxygen content corresponding to this point is read off the abscissa and the accuracy evaluated. A determination takes 15-18 hours when the x-ray tube is operated under ordinary conditions.

SUMMARY

Preparations of the lower oxides of titanium have been synthesized containing from 0 to 17% wt of oxygen. It has been found that the homogeneity region of the lower oxides of titanium extends up to a composition corresponding to $TiO_{0.48}$ (14.4% wt. oxygen).

The relationship between the lattice constant c and the oxygen content of the lower oxides has been used for the quantitative determination of oxygen in the lower oxides of titanium by a radiographic method, with an accuracy of ± 0.1% wt.

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THE POLAROGRAPHY OF THE NOBLE METALS (A REVIEW)

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The first successes in the field of the polarographic determination of the noble metals have mainly been achieved in the course of the last few years. The use of a dropping mercury electrode is connected with some difficulties which are specific for the noble metals. A large number of the complex compounds of the noble metals are reduced by metallic mercury, and this chemical interaction does not permit their polarographic determination. In the case of the other complex compounds, the main obstacle to their electrical reduction within the potential limits used in polarography as their high stability. The platinum metals (with the exception of palladium) possess the capacity to depress the hydrogen overvoltage on mercury, and this leads to the development of catalytic hydrogen waves which mask the waves which arise as the result of the reduction of the platinum metal, or which complicate their interpretation.

The difficulties indicated have been overcome mainly by adopting one of the following approaches:

a) choosing a reagent which forms a complex compound with the noble metal, which is not reduced by mercury and gives a diffusion current in a potential region more positive than the reduction potential of the supporting electrolyte;

b) by using the catalytic current of hydrogen which, in certain cases, is proportional to the concentration of the platinum metal;

c) by replacing the dropping mercury electrode by an electrode made from a more noble metal, e.g., platinum.

Towards the end of 1957 the oscillographic comparative titration method was suggested for the determination of some of the platinum metals [1].

Each of the approaches just mentioned has its advantages and disadvantages; accordingly, in choosing the method to be adopted, each particular case must be judged separately on its own merit.

The present article is a brief review of the work carried out on the polarography and amperometry of the noble metals, which has been published up to the end of 1958.

The half-wave potentials of the noble metals in various supporting electrolytes, and schemes for the electrode processes, for a large part of the work published up to the end of 1955, have already been incorporated in A Table of the Half-Wave Potentials of Inorganic Depolarizers" compiled by Vlcek [2].

Gold. Hrman [3] during a study of the behavior on a dropping electrode of the complex compounds formed during the interaction of $HAuCl_4$ with excess Na_2SO_4, Na_2HPO_4, $NaHCO_3$, KSCN, KCN, and KOH established that only $KAu(OH)_4$, $KAu(CN)_4$, $KAu(CN)(OH)$ and $KAu(CN)_2$ are sufficiently stable to reduction by metallic mercury. For analytical purposes he suggested the use of potassium hydroxocyanoaurate, and recommended his technique for the determination of gold in ores. A subsequent check on this method [4-6] showed that this method is not suitable for the determination of small amounts of gold, and that it is better to use the complex hydroxy compounds of trivalent gold. Polarographic determination of gold in the form $KAu(OH)_4$ in the presence of gelatin, has been recommended for the determination of gold in silver [4, 5], in industrial cyanide solutions, sludge, and assay beads [6-7] and in ruby glass [8].

A group of Czech workers have confirmed the possibility of determining gold in the form of complex hydroxy compounds [9]. Of special interest is the possibility which they established of polarographing gold from solutions of ethylenediamine [10], ethyelenediamine tartrate [11], and a combination of the latter with complexons [12], or with sodium pyrophosphate [13]. A mixture of ethylenediamine tartrate and sodium pyrophosphate [13] has made it possible to develop a method for the selective polarographic determination of gold, in which only metals which are reduced at more positive potentials (Hg, Ag, and Pt) interfere. In all probability this method will be used for the analysis of gold-containing materials with a large content of impurities (alloys, concentrates, sludges, etc.).

Gutman and Schober [14] while carrying out a polarographic study in anhydrous ethylenediamine containing $NaNO_3$ as the supporting electrolyte, obtained a wave for the reverse reduction of Au (III). The current is proportional to concentration over the range 10^{-1} to 10^{-3} M.

A number of authors have shown that it is possible to obtain polarographic waves for gold on a stationary platinum electrode [15-16], and on a rotating microelectrode [17]. In the case of the latter, the diffusion current which corresponds to the reduction of Au(III) to the metal, is proportional to the gold concentration from 1×10^{-5} to 3×10^{-3} M.

Platinum. Herasymenko and Slendyk [18], and Slendyk [19] have suggested a method for the polarographic determination of traces of platinum in palladium on the basis of the catalytic hydrogen wave, the height of which is approximately proportional to the platinum concentration in solution. The most satisfactory results were obtained at a concentration of 2 M with respect to HCl, and at a platinum concentration from 10^{-6} to 10^{-7} M.

The choice of a complex compound of platinum which would be suitable for its polarographic determination on a dropping electrode has proved very difficult. It has been found that it is impossible to get polarographic waves for the complex chlorides and bromides of di- and quadrivalent platinum [20]; and for cyanides of Pt^{II} [20-21]; complexes with ammonia, ethylenediamine [21]; and pyridine [21-22]. Subsequently, however, Rius an and Molera [23] obtained clearly defined polarographic waves during the reduction of the complex cyanides of quadrivalent platinum.

English [24] has developed a method for the polarographic determination of platinum in an organic catalyst using as a supporting electrolyte a mixture of citric acid and sodium hydrophosphate (pH 7). Under such conditions, a reduction wave for Na_2PtCl_6, which has a somewhat unusual shape, starting at zero applied emf and finishing around -0.6 volt (saturated calomel electrode) is obtained. The wave height is measured at a point corresponding to -0.3 volt. The experimental accuracy is 0.2% for a platinum content of 3.5 mg in 50 ml of solution.

Laitinen and Onstott [25] have shown that the ion $[PtCl_4]^{2-}$ is adsorbed on the electrode and is thereafter reduced on the electrode at low emf values.

Scarano [26] obtained a wave for H_2PtCl_6 in a supporting electrolyte of saturated NaCl, with three diffusion regions. The height of the first, and also the total height of the second and third waves was found to be linearly related to the platinum concentration.

Simpson, Evans, and Saroff [27] have established that it is possible to get a wave for quadrivalent platinum in a supporting electrolyte of an acetate buffer solution. Values of the diffusion coefficients for noble metal ions as calculated by means of the Ilkovich equation are included in their paper.

Of interest is a study of the behavior of certain complex compounds of quadrivalent platinum, including those with: hexamine and triethylenediamine [28], the halogeno- and hydroxy pentamines [29], and also the tetramines of divalent platinum [30], and compounds containing 1, 10-phenanthroline [31]. In a supporting electrolyte of KCl and KNO_3, and also in KNO_3 in the presence of NH_4OH, platinum (IV), in solutions of the first two compounds, is reduced to the divalent state, while at potentials more negative than -1.3 volt (saturated calomel electrode) it is reduced to the metal. Clearly defined waves are obtained, in which the diffusion current is proportional to the platinum concentration. The hydroxy- and chlorpentamine complexes of platinum behave in similar fashion. On replacing the molecule of NH_3 in $[Pt(NH_3)_6]^{4+}$ by a halogen there is observed a shift in $E_{1/2}$ to more negative values. A study of the ions of platinum tetramine has shown that the trans-isomer is reduced more readily than the cis-isomer.

Beran and Dolezal [32] using a supporting electrolyte consisting of a mixture of ethylenediamine tartrate and thiocyanate, obtained a reduction wave for $[Pt(en)(CNS)_2]$ the height of which was proportional to the platinum concentration within the limits 4×10^{-5} to 3×10^{-3} M. Chlorides, nitrates, sulfates, and Complexon III do not interfere. Fe^{3+} forms a precipitate which adsorbs the platinum. Cu, Te, Ce, Pd, and Au complicate the determination. The experimental error is ± 4%. The drawback of the method is the long time taken to form the ethylenediaminethiocyanate of divalent platinum (12 hours).

Bardin and Lyalikov [33-34] were the first to show that it is possible to use solid platinum electrodes for the determination of platinum. In a supporting electrolyte of 0.1 N $NaNO_3$, platinum, in the form of H_2PtCl_6, is reduced to the metal at + 0.3 volt (saturated calomel electrode). The diffusion current is proportional to the platinum concentration. The experimental accuracy is + 7%. The effect of foreign ions has not yet been studied.

Palladium. Willis [21] has studied in detail the polarographic behavior of complex compounds of palladium with potassium cyanide, ammonia, pyridine, and ethylenediamine. Within a certain concentration range (not more than 5×10^{-3} M), the author obtained clearly defined waves which can be used for analytical purposes. The author has pointed out that with increasing basic properties of the amine, $E_{1/2}$ becomes more negative, while the reduction becomes less reversible.

Rius and Molera [23] in contradicting the results of Willis, have noted that palladium is not reduced on a dropping electrode from a solution of cyanide.

Wilson and Daniels [35] having studied the conditions for the polarographic determination of palladium in an ammoniacal supporting electrolyte (i.e., in the form $[Pd(NH_3)_4]^{2+}$, established that platinum and appreciable amounts of rhodium, iridium, and gold affect the diffusion current of palladium and have recommended that palladium be precipitated beforehand with dimethylglyoxime.

Simpson, Evans, and Saroff [27] obtained a clearly defined wave for palladium starting at an applied emf of 0 volt on using a supporting electrolyte of acetate buffer and 0.06 M HCl.

Depending on the acetate and chloride concentrations, the diffusion coefficient of the $[PdCl_4]^{2-}$ ions was found to vary within the limits $0.4\text{-}0.8 \times 10^{-5}$ $cm^2\ sec^{-1}$.

Linhart [36] has suggested a method for the polarographic determination of palladium in the presence of gold and platinum in a supporting electrolyte of lithium hydroxide. The method permits palladium to be determined in alloys with gold ("white gold") with an accuracy of ± 1%, and also palladium and gold in an alloy with platinum.

Tomicek and co-workers [9-10] have investigated the possibility of determining palladium polarographically in a supporting electrolyte of hydroxides and various amines. Ethylenediamine tartrate was found to be a particularly valuable supporting electrolyte, this permits determination of gold and palladium in each others presence. The use of ethylenediamine tartrate in conjunction with various complexons [11-13] permitted a method to be developed for the determination of palladium in the presence of Pb^{2+}, Cd^{2+}, As^{3+}, Sb^{3+}, Sn^{2+}, WO_4^{2-}, MoO_4^{2-}, Fe^{3+}, Zn^{2+}, Sn^{4+}, Cr^{3+}, Co^{2+}, Mn^{2+}, and U_2^{2+}; Cu^{2+} and Bi^{2+} interfere.

Bardin and Lyalikov [37] have shown that it is possible to determine palladium polarographically by using platinum stationary and rotating electrodes. Under certain conditions, the waves obtained can be used for analytical purposes. The experimental accuracy is about ± 3% for palladium concentration limits of 5×10^{-5} to 2×10^{-2} M.

Iridium. Numerous attempts to obtain current–voltage curves for iridium on a dropping mercury electrode have not met with success, since most of the complex compounds of quadrivalent iridium, on coming into contact with mercury, are reduced to trivalent iridium compounds; the latter are not usually reduced at potentials preceding the reduction potential of the supporting electrolyte. Accordingly, Willis [21] who tried out complex compounds of iridium with potassium cyanide, potassium thiocyanate, ammonia, pyridine, and ethylenediamine for polarographic purposes, and Repin [22] who tried sodium chloride, sodium phosphate, Seignette salt, and tetraethylammonium iodide as supporting electrolytes for the polarographic determination of iridium (III), were unsuccessful. The polarographic curves of iridium (IV) in a supporting electrolyte of sodium chloride and gelatin, which West, Dean, and Breda obtained [38], were so nebulous in form that the authors themselves did not study them any further. Recently, Pshenitsyn, Ezerskaya, and Ratnikova [39] obtained curves for the reduction

of the chloroiridate ion, and oxidation curves for the chloroiridite ion, on a rotating platinum electrode. The diffusion current of iridium (IV) corresponding to its reduction to the trivalent state, is proportional to the iridium concentration, and permits the latter to be determined within the limits 2×10^{-3} to 5×10^{-6} M. iridium. The experimental accuracy is ± 5%. Rhodium, platinum, palladium and several non-noble metals do not interfere with iridium determination.

Rhodium. Willis [40] who has studied in detail the reduction of a large number of the complex compounds of Rh (III) on a dropping mercury electrode, found that some of them $[Rh(CN)_6]^{3-}$, $[Rh(NH_3)_5Cl]^{2+}$, $[Rh(CNS)_6]^{3-}$ and $[RhPy_6]^{3+}$ form clearly defined polarographic waves whose height is proportional to the rhodium concentration of the solution. The author is of the opinion that the best of these compounds for quantitative determination is $[RhPy_6]Cl_3$.

Repin [22] has also used the pyridine compound of rhodium (III) for determination of rhodium, but attributed another composition to the complex $[RhPy_5Cl]Cl_2$. Iridium in any amount, and platinum in equal amounts to rhodium, do not interfere with the determination of rhodium in a pyridine supporting electrolyte (more than 0.001 g/liter). An oscillographic method for the determination of rhodium suggested by Beran and Dolezal [41] has proved very promising. In a supporting electrolyte of 0.1 M HCl + 0.6 M NaCl, in the presence of rhodium there is formed a characteristic sharp peak in the anodic part of the curve. The peak height is linearly related to the rhodium concentration (from 0.5 to 25 γ of rhodium in 20 ml solution). The method described can be used for the determination of rhodium in the presence of 2000-3000 times its amount of platinum, palladium, and gold with reasonable accuracy.

Quite a few papers have been published on the study of the polarographic behavior of rhodium. However, the complex fluorides [38], chlorides and nitrates [42] studied are insufficiently stable with respect to mercury, and are, apparently, not very suitable for analytical purposes. The biscyclopentadienyl of trivalent rhodium $[Rh(C_6H_5)]X_2$ [43] is reduced on the dropping electrode; nevertheless, because of the difficulty of preparing it, it does not seem to have much promise for analytical use.

Ruthenium. It has been established by Willis [21] that it is impossible to reduce on a dropping mercury electrode the solutions of the complex cyanides, thiocyanate, and ammines (NH_3 and Py) of tri- and quadrivalent ruthenium, because of the stability of these compounds. On the other hand, the complex chloride of Ru (IV) is reduced on coming into contact with mercury. In order to find reduction waves for ruthenium, Niedrach and Tevebaugh [44] chose a non-complex compound—ruthenium perchlorate (IV). In a supporting electrolyte of 0.1-5 N $HClO_4$, they obtained three well shaped curves, one of which can be used for the quantitative determination of ruthenium, as long as conditions can be found for converting the ruthenium quantitatively into the perchlorate. Recently, Brancia, and Mesaric [45] obtained in a supporting electrolyte of oxalic, tartaric, and citric acids, reduction waves for ruthenium which are proportional to the ruthenium concentration within the limits 4 to 120 γ/ml. Unfortunately, the authors have not established the valence of the ruthenium before and after reduction, nor the character of the ruthenium compound with the hydroxy acids. Silverman and Levy [46] who studied the oxidation and reduction of compounds of sexi, septi-, and octivalent ruthenium K_2RuO_4, $KRuO_4$, and RuO_4 (in a supporting electrolyte of $NaClO_4$), and also De Ford and Davidson [47] who studied the oxidation of the complex cyanides of di- and trivalent ruthenium, used a platinum electrode instead of a dropping mercury electrode, and obtained well shaped current—voltage curves. The authors of these articles, who were not carrying out this work for analytical purposes, nevertheless pointed out [46] that there is a proportionality between the current and the ruthenium concentration within the limits 6×10^{-4} to 1.2×10^{-3} M. Further checking and study of the reduction conditions, probably could lead to the use of some of these electrode reeactions for the quantitative determination of ruthenium. However, neither the ruthenate or the perruthenate, because of their instability, nor the cyanides because of the difficulty of preparing them, can be regarded as compounds which are suitable for the determination of ruthenium within the general scheme of the analysis of the platinum metals. This is true to an even greater extent to the determination of ruthenium (on a dropping mercury electrode) in the form of ruthenocene $Ru(C_5H_5)$ and its salts which give reduction and oxidation waves a in a supporting electrolyte of $NaClO_4$ [48]. Since, according to the observations of Heyrasymenko and Slendyk [49], the catalytic waves of hydrogen formed in the presence of ruthenium are particularly large, they can be used for the determination of very small amounts of ruthenium. El Guebely [50] who measured the hydrogen catalytic wave in solutions of $Ru_2(SO_4)_3$ in 0.01 N H_2SO_4 and 0.1 N Na_2SO_4, determined the extremely small amounts of ruthenium of 2×10^{-7} - 5×10^{-10} mole/liter. The linear relation between the current and the concentration is

preserved in the concentration range indicated with an accuracy of 5-10%, but breaks down on increasing the ruthenium concentration. Susic [51] determined ruthenium on the basis of the catalytic currents which develop in the presence of a mixture of tri- and quadrivalent ruthenium in a solution of 0.9 M $HClO_4$, in a solution of 0.1 M Complexon II (pH > 5) or 0.05 M Complexon II and 0.5 M ammonium acetate. The author recommends the first supporting electrolyte for the determination of from 0.01 to 0.37 γ/ml of Ru, and the second and third for the determination of more than 0.1 γ Ru/ml. It should be pointed out that Susic's results do not agree with the results of Niedrach and Tevebaugh [44], who obtained reduction waves for tri and quadrivalent ruthenium in a supporting electrolyte of $HClO_4$, but no catalytic waves for hydrogen.

Osmium. Crowell, Heyrovsky, and Engelkemeir [52] were the first to study the reduction of osmium on a dropping electrode. These authors established that it is impossible to determine osmium tetroxide or its compounds in acid solutions polarographically because of their interaction with metallic mercury. Polarographic determination is only possible in alkaline solutions; the best results were obtained by these authors in a supporting electrolyte of saturated solutions of $Ca(OH)_2$ and $Ba(OH)_2$. The polarograms thereby obtained have three diffusion regions corresponding to the successive reduction of Os (VIII) to Os (VI), Os (IV), and Os (III), and can be used for the quantitative determination of osmium at concentrations of the latter of the order of 10^{-4} M. Subsequently, these results were confirmed by Meites [53] coulomometrically. Meites also studied in detail the reduction of osmium (VIII) in a supporting electrolyte of mineral (phosphoric, sulfuric, hydrochloric, and perchloric acids) and organic (tartaric and citric) acids, in some buffer solutions, in an ammoniacal solution of ammonium chloride, and in potassium cyanide and potassium thiocyanate. In the author's opinion, osmium is best determined polarographically in cyanide solutions. Rius and Molera [23] had previously obtained reduction waves for Os (VI) in a supporting electrolyte of KCN.

Kolthoff and Parry [54] used for the polarographic determination of osmium the catalytic wave for the decomposition of hydrogen peroxide which develops as the result of the following reactions:

$$Os(VIII) + 2e \rightarrow Os(VI) \qquad Os(VI) + 2H^+ + H_2O_2 \rightarrow Os(VIII) + 2H_2O$$

The wave height, which depends on both the osmium concentration and the hydrogen peroxide concentration, is measured according to the current which arises at a potential of +0.23 volt with respect to the saturated calomel electrode.

Amperometric Titration

a) Using a Dropping Mercury Electrode. Kolthoff and Langer [55] have used α-nitroso-β-naphthol for titrating palladium. The titration was carried out in an acetate buffer solution at a potential of -0.6 volt (saturated colomel electrode), under which conditions both palladium and the reagent give diffusion currents.

Tomicek and co-workers [56] established that it is possible to titrate palladium amperometrically with dimethylglyoxime, salicylaldoxime, 8-hydroxyquinoline, and mercaptobenzothiazole. Best results were obtained with dimethylglyoxime. Titration was carried out in a short circuited system (at 0 volt applied emf) in a supporting electrolyte of an acetate buffer solution or 0.1 N HCl, 0.05 N HNO_3, and 0.1 N KNO_3. The experimental accuracy is about 2%. Large amounts of gold interfere; Ag^+, Cd^{2+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+} etc. do not interfere.

Wilson and Wilson [57] have recommended 1, 2, 3-benzotriazole for titrating palladium. Pt, Rh, Ir and a number of nonnoble metals do not interfere with titration by this reagent. Os, Ru, Au, Fe, and Ni interfere. The experimental accuracy for determination of palladium is ± 0.3%.

Milenko and Susic [58] have titrated gold (III) in H_2SO_4 solution at 0 volt by means of ascorbic acid.

b) Using a Rotating Platinum Electrode. Ezerskaya [6] has suggested a method for titrating gold (at 0 volt applied emf) using sodium thiosulfate or mercaptobenzthiazole. The first reagent permits determination of gold at a concentration of the order of 10^{-5}, while the second permits determination of 10^{-6} mole/liter with completely satisfactory accuracy. Iron and large amounts of copper interfere. Interference from iron can be suppressed by adding KHF_2.

Reishakhrit and Sukhobokova [59] have developed a method for the determination of gold in the presence of palladium, selenium, and tellurium by titration with hydroquinone. The titration was carried out at a potential of +1.0 volt in a supporting electrolyte of 2 N H_2SO_4 at 60°. The end point was established on the basis of the increasing wave for the oxidation of hydroquinone. For gold contents of 10^{-2} to 10^{-4} mole/liter, the experimental accuracy varies from 1 to 10%.

Bardin and Lyalikov [60] have shown that palladium can be titrated amperometrically with α-furildioxime, while Bardin and Melika [61] have shown that β-furfuraldoxime can be used. For palladium contents ranging from 10^{-4} to 10^{-2} mole/liter, titration can be carried out with an accuracy of 2-3%.

Pshenitsyn and Ezerskaya [62] have suggested a method for the amperometic titration of iridium with hydroquinone or ascorbic acid, for iridium contents ranging from 0.002 to 1.0 mg of iridium per ml. Only gold and large amounts of ruthenium and iron interfere with the titration of iridium under the conditions chosen.

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A RAPID MICROMETHOD FOR THE DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

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The problem which confronted us was to search for a simple micromethod for determining halogens, both in monomers and polymers, which would require simple apparatus and would be suitable for compounds containing other elements in addition to halogens.

Many microanalytical methods are known for the determination of halogens in organic compounds; catalytic oxidation by combustion of test material in an oxygen stream using a platinum catalyst [1]; the Carius method [2]; fusion of the test material with potassium metal [3]; combustion of the organic material in a stream of oxygen, the halogen being trapped by silver metal [4] with simultaneous determination of carbon, hydrogen, and halogen. All these methods require fairly complicated apparatus, and, with the exception of the last method, it is necessary to transfer the test halogen into another vessel.

Of interest is the rapid micro method of determining halogens suggested by Schoniger [5] which is carried out in a simple apparatus. Combustion of the organic test material is carried out in a flask filled with oxygen, the halogen liberated being then titrated in the same flask.

Combustion of a material in vessels filled with oxygen was first suggested in 1892 by Hempel [6] for the macrodetermination of sulfur in coal and other organic materials; the method was subsequently improved in coal and other organic materials; the method was subsequently improved by Graefe [7] and Marcusson and Doscher [8]. The latter determined halogens also by this method. This method, however, did not find wide application since combustion was carried out in flasks of too large a volume amounting to 6-10 liters, which often cracked. In 1922 Votocek [9-11] developed this method further and used it for the determination of chlorine in organic materials. Later, Mikl and Pech [12, 13] determined halogens and sulfur, both independently, and in each other presence, in organic materials.

All the variants mentioned above for the determination of halogens and sulfur by combustion in a vessel filled with oxygen were used for macroaliquots of 0.5-0.1 g. Schoniger [5], for the microdetermination of halogens, cut down the weight of sample to 4-8 mg and the capacity of the flask to 300 ml. Chlorine and bromine were determined acidimetrically by Viebock's method [14] using mercury cyanate.

For halogen determination we modified the construction of the flask, since the flasks used by Schoniger have some essential drawbacks. We used conical or flat bottomed flasks with a side arm and a tap for connecting to the atmosphere. The ground glass stopper had a drawn out end so that it was possible to fuse a platinum wire* into it.

Chlorine and bromine were determined by titrating with mercuric nitrate or perchlorate, while iodine was determined as the iodate by Leipert's method [15] using sodium thiosulfate as titrant.

*A flask without a side arm (as used by Schoniger) is not suitable to work with. It is sometimes impossible to remove the stopper on account of the vacuum which develops in the flask after absorption of the combustion products. The use of a stopper with a drawn out end, as in our construction, makes it easy to fuse the platinum wire into it without damaging the stopper.

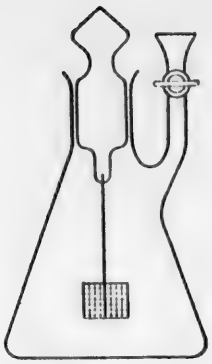

Fig. 1

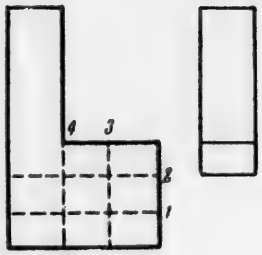

Fig. 2

Fig. 3

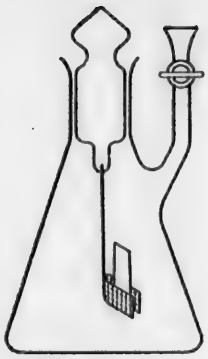

Fig. 4

An aliquot of the halogen-containing organic material is wrapped up in ashless filter paper and the latter fastened to the platinum wire fused into the drawn out end of the stopper; the latter is rapidly ignited in the flask filled with oxygen. The halogen thereupon is quantitatively converted to the hydrogen halide which is absorbed by a solution of alkali. The halogen is titrated in the same flask.

Apparatus. Determination is carried out in a conical or flat bottom flask made of heat-resistant glass, and with a capacity of 200-350 ml; the flask is fitted with a ground glass stopper and is provided with a side arm. The latter is provided with a tap and terminates in a funnel (Fig. 1). The bottom of the stopper is drawn out, and into the drawn out end is fused a platinum wire 70-80 mm long and 0.7-0.8 mm in diameter, depending on the height of the flask used. The platinum wire should not get closer than 20-30 mm to the bottom of the flask. To the end of the wire is fastened a platinum grid 20× 30 mm in size; the grid is attached to the wire either by bending the latter or by welding it on.

Ashless filter paper made by the D. I. Mendeleev Moscow Chemico-Technological Institute was used for combustion of the test materials; the shape and size of the filter papers are shown in Fig. 2. For analysis of liquids, capillary tubes with a small expanded portion in the middle, or without such an expanded portion, were used, the latter being fused at one end (Fig. 3).

Experimental Procedure. An aliquot of solid test material (3-15 mg, in certain cases up to 50 mg depending on the halogen content), is weighed out by difference from a weighing tube onto the center of the filter paper; the latter is then carefully wrapped up by folding along the dotted lines (Fig. 2).

Nonvolatile liquids are taken in capillaries. It is useful to seal one end of such capillaries with a small piece of paraffin wax, since the latter helps complete conversion of the halogen into the hydrogen halide and also prevents loss.

The capillary plus test material are also wrapped up in filter paper in such a way that the open end of the capillary is covered by several layers of paper.

The sample is wrapped up in the filter paper as if it were a little parcel . The parcel is fitted into the platinum grid, so that the long narrow end of the filter paper is pointing upwards (Fig. 4). The lower part of the platinum grid is bent upwards slightly so that the sample is held securely in position and its complete combustion is ensured.

Determination of Chlorine and Bromine. 10 ml of distilled water, 1 ml of 2 N potassium hydroxide, and 3 drops of hydrogen peroxide are placed in the flask for absorbing the halogen. In order to expel the air from the flask, oxygen is passed into it from a cylinder, through a flask containing 50% potassium hydroxide, for 2-3 minutes at the rate of 100-120 ml per minute. The upper end of the filter paper is then ignited and the stopper rapidly inserted in the flask. During the combustion process, which lasts 15-20 seconds, the flask should be left at rest, the stopper must, however, be firmly kept in position by hand in order to prevent the gases formed from forcing it out.

When combustion is complete, in order to accelerate absorption of the combustion products, the flask is vigorously shaken for 6-10 minutes until the cloud over the liquid in the flask has disappeared completely.

TABLE 1

Test material	Sample weight, mg	Chlorine content, %		Deviation, %
		found	theoretical value	
Lead triphenylchloride	4,025	7,50	7,50	±0
$(C_6H_5)_3$ PbCl	5,200	7,29		−0,21
Dithoxylylchorohydrinxylithane	5,345	7,67	7,69	−0,02
$C_{19}H_{21}S_2O_7Cl$	4,805	7,79		+0,10
Lead diphenydichloride	4,045	16,07	16,40	−0,33
$(C_6H_6)_2PbCl_2$	4,375	16,27		−0,13
Sodium p-chlorobenzene sulfonate	3,920	16,23	16,52	−0,29
	5,640	16,30		−0,22
$C_6H_4ClSO_3Na$				
Dinitrochlorobenzene	4,550	17,38	17,50	−0,12
$C_6H_3Cl(NO_2)_2$	24,365	17,31		−0,19
p-Chlorophenylmethacrylamide	3,050	18,33	18,12	+0,11
$ClC_6H_4NHCOC_3H_5$	4,620	18,38		+0,16
p-Nitrobenzylchloride	4,390	20,97	20,66	+0,31
$C_6H_4CH_2NO_2Cl$	4,860	20,90		+0,24
p-Thiocyanochlorobenzene	5,640	21,17	20,90	+0,27
C_6H_4ClCNS	5,275	21,09		+0,19
	3,560	20,90		±0
Aminoxylithane hydrochloride		21,11	20,91	+0,20
$C_5H_{12}O_3NCl$		21,21		+0,30
p-Chloronitrobenzene	2,785	22,59	22,52	+0,06
$C_6H_4NO_2Cl$	4,265	22,69		+0,16
p,p'-Aminochlorodiphenyl	5,380	17,55	17,39	+0,16
$(C_6H_4)_2NH_2Cl$	4,705	17,20		−0,19
Chlorbenzoic acid	7,640	22,87	22,64	+0,23
ClC_6H_4COOH	6,095	22,93		+0,29
p-Chlorphenol	3,365	27,66	27,62	+0,04
$C_6H_4(OH)Cl$	3,940	27,78		+0,16
p-Chloroaniline	3,950	27,59	27,93	−0,34
$ClC_6H_4NH_2$	3,670	27,58		−0,35
Semicarbazide hydrochloride	4,280	31,84	31,78	+0,06
$H_2NCONHNH_2HCl$	5,055	31,80		+0,02
Aminoguanidine hydrochloride	3,675	32,14	32,07	+0,07
$C\begin{matrix}\diagup NH-NH_2 \\ =NH\cdot HCl \\ \diagdown NH_2\end{matrix}$	3,540	32,18		+0,11
2,3-Dichloro-4,5-dimethylstyrene	3,410	35,05	35,28	−0,23
$C_6H_4(CH_3)_2Cl$	3,580	34,94		−0,34
2,4,6-Trichlorophenylmetacrylamide	2,645	40,42	40,22	+0,20
$Cl_3C_6H_2NHCoC_3H_5$	4,000	40,19		−0,03
Tetrachlorophthalic acid	2,925	45,42	45,37	+0,05
$C_6Cl_4(COOH)_2{}^1/_2H_2O$	3,450	45,33		−0,04
Tetrachlorophthalic anhydride	4,065	49,28	49,25	+0,03
$C_6Cl_4C_2O_3$	3,300	49,63		+0,38
2,4,5-Trichlorotoluene	4,540	54,34	54,41	−0,07
$Cl_3C_6H_2CH_3$	2,930	54,13		−0,28
Hexachlorobenzene	3,845	74,47	74,70	−0,23
C_6Cl_6	3,260	74,54		−0,16

Unless the flask is shaken, absorption of the combustion products may take 45-60 minutes. Before opening the flask, a small amount of distilled water is poured into the side arm and into the throat surrounding the stopper. The vacuum in the flask is destroyed by opening the tap in the side arm, the stopper is then easily lifted out. The stopper and platinum wire plus grid are carefully washed with distilled water over the flask.

TABLE 2

Test material	Sample weight, mg	Chlorine content found, %		
		in a flask filled with O_2	in O_2 current	by fusion with potassium
Copolymer of isoprene and chlorostyrene, Sample IVS* No. 13	5,290	13,42	—	—
	4,440	—	13,44	—
The same No. 25	2,910	24,55	—	—
	34,590	—	—	24,21
The same No. 32	5,670	11,05	—	
	7,860	—	10,98	
The same No. 34	3,515	11,12	—	—
	3,020	11,10	—	—
	5,460	—	10,96	—
The same No. 35	5,425	17,51	—	—
	5,060	17,82	—	—
	6,285	—	17,82	—
The same No. 39	5,490	22,82	—	—
	5,295	22,93	—	—
	3,245	—	22,63	—
	4,455	—	22,92	—
Three-dimensional polymer Mark KFUKh, Sample* No. 25	4,400	9,45	—	—
	4,520	9,57	—	—
	27,845	—	—	9,25
The same No. 1	2,685	10,61	—	—
	26,670	—	—	10,61
The same No. 2	4,140	10,80	—	—
	3,115	10,93	—	—
	36,940	—	—	11,19
The same No. 4	4,225	10,50	—	—
	5,060	—	10,73	—
Polychlorovinyl	4,450	56,35	—	—
	3,470	56,43	—	—
	3,115	—	56,42	—
	3,305	—	56,23	—
Chloride residue in treated chitin	39,960	0,23	—	—
	51,310	0,18	—	—
	35,435	—	—	0,28
	28,290	—	—	0,22
The same No. 32	40,010	0,33	—	—
	44,730	0,34	—	—

*A sample prepared in the Institute of High Polymer Compounds.

In order to decompose the hydrogen peroxide, the flask is boiled for 5 minutes, the solution is then cooled and acidified with 0.5 N nitric acid to a pH of 2.3-2.5*. The total volume of liquid in the flask before titration is 20-25 ml. Titration is carried out in the same flask as that used for the combustion; titration is carried out with 0.01 N mercuric perchlorate** or nitrate in the presence of 2-3 drops of a 1% solution of diphenylcarbazone to the appearance of a weak rose color.

*The amount of nitric acid taken is sufficient to neutralize the alkali completely and to leave 0.5 ml of acid in excess. For new solutions of alkali and acid, the amount of nitric acid required for neutralizing the alkali to the phenolphthalein endpoint is determined anew.

**0.01 N $Hg(ClO_4)_2$ is prepared by dissolving, on heating, 1.1 g of HgO in 4 ml of 30% $HClO_4$. The solution is diluted with 50 ml of water and filtered, the filter is carefully washed and the volume made up to 1 liter with distilled water.

TABLE 3

Test material	Sample weight, mg	Bromine content, % found	Bromine content, % theoretical	Deviation, %
Methylbromophthalimide	5,000	33,24	33,21	+0,03
$BrCH_3C_8H_2O_2NH$	4,435	33,03		−0,18
Dimethylbromostyrene	2,745	37,81	37,91	−0,10
$(CH_3)_2BrC_6H_2CH=CH_2$	2,550	37,62		−0,29
p-Bromonitrobenzene	3,500	39,58	39,55	+0,03
$BrC_6H_4NO_2$	4,545	39,48		−0,07
p-Bromobenzoic acid	3,085	39,81	39,72	+0,09
BrC_6H_4COOH	3,305	39,54		−0,18
2,3,3-Trimethylpentene-1-bromo-5	2,660	41,88	41,91	−0,03
$C_8H_{15}Br$	2,840	42,00		+0,09
5,7-Dibromo-8-hydroxyquinoline	2,895	52,80	52,75	+0,05
$Br_2C_9H_4(OH)N$	3,610	52,74		−0,01
p-Dibromobenzene	5,605	67,45	67,74	−0,29
$C_6H_4Br_2$	5,110	67,63		−0,11

TABLE 4

Test material	Sample weight, mg	Iodine content, % found	Iodine content, % theoretical	Deviation, %
Sample No. 281	4,775	25,75	25,67	+0,08
$C_{22}H_{27}ON_2SI$	4,050	25,46		−0,21
Sample No.366	3,745	26,22	26,24	−0,02
$C_{21}H_{29}ON_2SI$	3,015	26,43		+0,19
Sample No. 207	2,190	27,25	27,13	+0,12
$C_{20}H_{25}ON_2SI$	3,315	26,89		−0,24
α-(Nitrofurylpropyl) methylquinoline iodide	4,380	29,95	29,92	+0,03
$C_{17}H_{17}NNO_3OI$	4,140	29,90		−0,02
Iodoalkylate-1-methyl 2 (p-tolyl) benzimidazol	3,780	34,61	34,85	−0,24
$C_{16}H_{17}N_2I$	3,690	34,61		−0,24
m-Iodobenzoic acid	3,460	52,27	51,39	−0,12
IC_6H_4COOH	4,090	51,24		−0,15
β-Iodopropionic acid	9,250	63,40	63,47	−0,07
ICH_2CH_2COOH				

Determination of Iodine. For the determination of iodine, the liquid used for absorption is 10 ml of distilled water with 1 ml of 2 N potassium hydroxide, no hydrogen peroxide being added as in the case of chlorine and bromine. Combustion is carried out as in the case of determination of chlorine and bromine. Iodine is determined by the Leipert method [15]—by oxidation of iodine to iodate, with subsequent titration of iodate with 0.02 N sodium thiosulfate, using starch as indicator.

It is necessary to carry out blank determinations with the solutions used in the actual determination (by combustion of filter without any sample) of the halogens. Results of the experiments described are given in Tables 1-4. One determination of a halogen using one flask takes 25 minutes. When four flasks are used, four determinations can be carried out in 1 hour. A shaker is recommended for shaking the flasks.

SUMMARY

The possibility has been demonstrated of introducing into the practice of organic microanalysis a rapid method for the determination of halogens (chlorine, bromine, and iodine) using sample weights of 3 to 15 mg; for low halogen contents the sample weight can be increased to 50 mg. The experimental accuracy is ± 0.3%.

The method consists of the combustion of test material, wrapped up in filter paper, in a flask filled with oxygen; the combustion products are absorbed with an alkali solution, and the halide is then determined titrimetrically in the same flask. The method can be used for both low molecular weight compounds and high molecular weight compounds which are difficult to burn. The presence of sulfur, of nitrogen in any form whatever, and of lead does not interfere with the determination. The method is distinguished by the simplicity of the apparatus used, and by the speed with which it can be carried out; it can be recommended for serial mass analysis.

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QUANTITATIVE DETERMINATION OF CH_2-GROUPS IN OPEN CHAINS CONTAINING NOT LESS THAN FOUR LINKS

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Determination of the individual components of more or less high molecular weight fractions of petroleum is impossible because of the astronomical number of possible isomers. The characteristicsof such mixtures can be given in the form of the relative content of various functional groups from which the molecules of the material studied can be constructed. For this purpose calculations are based on the average molecule of the fraction.

The methane-naphthenic part of the hydrocarbons of petroleum or bitumen can be characterized by the method of infrared spectroscopy in parts of the content of CH_3 and CH_2-groups. These groups are determined separately, mainly on the basis of the vibrations of the CH bond. Both the valence and the deformation CH-vibrations for CH_3 and CH_2-groups have different frequencies and are characterized by differences in the absorption intensity. The present article touches on the use of the deformation vibrations of the CH-bond for the quantitative determination of the content of CH_2-groups forming open chains with not less than four links (CH_2).

The deformation vibrations of the CH-bond in methylene groups appear in the region 800-700 cm^{-1} in the form of a wide absorption band. Normal paraffins in the liquid state give a single band at 720 cm^{-1}. In the case of crystalline, normal paraffins, liquid acids, and other compounds containing methylene chains, the band splits into two components [1, 2, 3].

The position of the absorption maximum depends [4] on the number of CH_2-groups in a continuous chain (Table 1).

Thus, molecules not containing chains of CH_2 groups with a number of CH_2 groups of four and more, do not give any absorption at 13.8-13.9 μ (725-720 cm^{-1}). Hastings and Anderson in 1951 suggested a method for the quantitative determination of all CH_2 groups in open chains by means of the integral absorption in the region 12.5-14.3 μ. This idea was used by Francis for the analysis of high molecular weight compounds [5]. The existence of a quantitative connection between the molecular absorption coefficient for this band and the number of CH_2-groups in the molecule has been pointed out in the collection of articles by West [6]. In order to carry out calculations on the basis of the method suggested for all the absorption region, obviously, one value should be a adopted for the group absorption coefficient.

However, actual results confirming this latter hypothesis are not available; its arbitrary nature is obvious.

We have made an attempt to investigate separately, from the point of view of quantitative determination, the absorption in the region 13.2-14.4 μ, i.e., to limit ourselves to determination of only CH_2-groups forming continuous chains containing not less than four links.

The work was carried out on a single beam apparatus IKS-11. The spectra were registered for a layer of 0.05 mm of the pure individual materials without using a solvent.

The area of the absorption band was measured on the curves relating optical density to wavelength, constructed by conversion. This area was that outlined by the optical density curve within the limits 13.3-14.4 μ and the "base line" produced as a tangent to the inflection points of the optical density curve. In Fig. 1 is shown the shape of the band, the recording of the apparatus, and the area measured.

TABLE 1

The Relation between the Characteristic Frequencies of the Deformation Vibrations of CH_2 Groups and Chain Length [4]

No. of CH_2 groups in the chain	Position of the absorption maximum (μ)
1	12.7-13.0
2	13.2-13.5
3	13.74
4	13.80
5	13.83
6	13.85
More than 6	13.86

The area was measured by means of transparent squared paper [7]. Calculation of the CH_2-groups content can be calculated in terms of one mole or 100 g of material. In order to show that the area S found is a measure of the CH_2-groups in a molecule, it is necessary to show that the value S/n is a constant (n is the number of CH_2-groups in a molecule). Bearing in mind that the measurements were carried out for one layer thickness for all materials, i.e., with a different number of molecules, it was necessary to refer the results obtained to an equal number of molecules in the layer. The number of molecules in the layer should be inversely proportional to the molar volume (the ratio of the molecular weight to the density of the M/d material can be arbitrarily taken as the molar volume. Thus the constant should have the value SV_M/n [8].

The results obtained are given in Table 2. The average group coefficient makes it possible to find the number of CH_2-groups contained in the average molecule of a fraction, as long as the molecular weight and the density are known; the number of CH_2-groups is the quotient obtained by dividing SV_M by this coefficient (equal to 204 in our case).

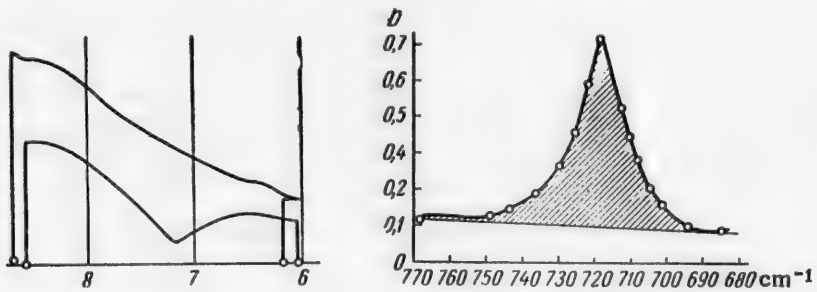

Figure. Dodecane, layer 0.05 mm; on the left—apparatus recorder chart with index lines [6, 7, 8], lined ready for calculation; on the right—optical density curve obtained by conversion.

The group absorption coefficient for solid materials differs appreciably from the coefficients for liquids; the calculated constant SV_M/n has a different value in the case of solid materials, the constancy of this value has not yet been established. The examples at our disposal are given in Table 3. Some authors are of the opinion that studies should only be carried out for the liquid phase, the solid materials being studied in the molten state. This position is rather indefinite since the absorption intensity should also depend directly on the temperature.

Calculation of the weight content of CH_2-groups in a given material is shown in Table 4. The constant calculating coefficient in this case will be

$$K = \frac{S}{cdx}$$

where c is the weight concentration of CH_2-groups (%); d is the specific gravity; and x is the layer thickness.

TABLE 2

Measurement of the Integral Absorption Intensity in the Region 13.2-14 μ for Calculation of the Number of CH_2-Groups in a Molecule

Test material	S, cm²	V_M	n	$\frac{SV_M}{n}$	$\Delta\frac{SV_M}{n}$	$\frac{\Delta n}{n}\cdot 100$
Heptane	7,35	149	5	219	+15	7,4
Octane	6,96	162,5	6	189	−15	6,3
Nonane	7,5	179	7	192	−12	6,0
Decane	7,7	195	8	188	−16	8,0
Undecane	9,35	212	9	221	+17	8,0
Dodecane	9,1	227	10	206	+ 2	1,8
Tridecane	9,25	244	11	205	+ 1	0,05
Pentadecane	9,30	276	13	197	− 7	0,35
Hexadecane	10,45	293	14	218	+14	0,70
Heptadecane	9,82	311	15	204	0	0
		$\frac{SV_M}{n}=204$			±10	3,8

TABLE 3

Measurement of the Integral Absorption Intensity in the Region 13.2-14 μ for Solid Materials

Test material	S	V_M	n	$\frac{SV_M}{n}$
$C_{36}H_{74}$	8.55	649	34	163
$C_{20}H_{42}$	8.0	364	18	162
Stearic acid $C_{17}H_{35}COOH$	7.85	336	16	164

In order to obtain the percentage weight content of CH_2-groups in an unknown material, it is necessary to divide S by Kdx, i.e., by 14.55 d (for a layer of 0.05 mm).

The results given in Tables 2 and 4 show that the mean error varies within the limits 0-8%, both for calculation of the number of groups in a molecule, and of the content by weight. The error amounts to ± one group for the determination of the number of groups. Experimental accuracy can be increased by more accurate measurement of the area, by careful purification of the standard materials and by increasing the number of individual materials examined. Thus, the methylene groups of paraffin chains can be determined quantitatively. The methylene groups of the naphthenic rings do not exhibit absorption in the given spectral region.

In order to evaluate the possibility of using the method considered in practice, synthetic mixtures of liquid methane and methane-naphthene hydrocarbons were made, and analyzed for their content of CH_2-groups (Table 5). In order to carry out calculations for mixtures, it is necessary to assume that the properties of the components making up the mixture are additive, and this can lead to some error. The specific gravity and the molecular weight assumed for calculating the concentration of CH_2-groups in mixtures were obtained as mean values on the basis of the assumption of additivity. The mixtures were prepared on a weight basis from the small number of individual materials at our disposal. The total amount of a mixture did not exceed 0.5-0.7 g.

The inconvenience, for purpose of calculation, of using the values of M and d, which in many cases, cannot be determined, is completely eliminated by studying the materials in solution. In this case the calculation is carried out on the basis of the appropriate conversion constant, established by carrying out measurements of

TABLE 4

Measurement of the Integral Intensity in the Region 13.2-14.4 μ for Calculation of the Percentage Weight Content of CH_2-Groups

Test material	S	c	d	$K=\frac{S}{cdx}$	$c=S/Kdx$	$\Delta c/c \cdot 100$
Heptane	7,35	70	0,684	3,08	74,1	5,9
Octane	6,96	63,7	0,703	2,69	68,0	7,7
Nonane	7,50	76,6	0,718	2,73	71,7	6,7
Decane	7,70	78,9	0,730	2,67	72,9	7,6
Undecane	9,35	80,8	0,741	3,12	86,2	6,7
Dodecane	9,1	82,5	0,751	2,94	83,0	0,6
Tridecane	9,25	83,7	0,757	2,92	83,7	0
Pentadecane	9,30	84,9	0,770	2,84	83,1	2,12
Hexadecane	10,45	85,9	0,774	3,14	92,5	7,7
Heptadecane	9,82	86,7	0,775	2,94	87,1	0,46
	Mean value			$K=2,91$	—	4,6

TABLE 5

Analysis of Synthetic Mixtures of Hydrocarbons for Their CH_2-group Content ($n \geq 4$)

Components of the mixture	Wt. ratio	d, mean	Molecular ratio 1 : 2	M, mean	ν measured	S	No. of CH_2-groups in a molecule		Percentage wt. cont., CH_2-groups	
							taken	found	ethyl-cyclo-hexane	dec-ane
Ethylcyclohexane Decane	1,335	0,765	1,69	124	162	3,02	2,97	2,4	33,8	26,8
Cyclohexane Dodecane	0,243	0,756	0,49	143	191	7,52	6,71	6,86	66,4	67,5
The same	1,780	0,772	3,60	103	131	3,33	2,18	2,14	29,6	29,2
Isooctane Dodecane	1,282	0,720	1,92	133	187	3,54	3,42	3,2	36,0	34,1
Ethylcyclohexane Dodecane Isooctane	1,767 4,230 1,000	0,748	1,73 2,74 0,96	144	192	6,07	5,06	5,71	49,9	55,8

the absorption of individual materials in solution. The number of the given groups in a liter of solution is determined directly; after this it is possible to convert into percentage by weight of groups, or number of groups in the material. Unfortunately, it is difficult to find an appropriate solvent for determination of CH_2-groups at 720 cm^{-1}; only carbon disulfide which does not absorb in this region might be suitable, and, possible, polyfluoroethylene. The absence of a solvent prevented us from carrying out this most interesting part of the work.

SUMMARY

It has been shown that it is possible to carry out a quantitative determination of long chain CH_2-groups by measuring the integral absorption in the region 13.3-14 μ.

A preliminary determination of the group adsorption coefficient is necessary, since it has different values for different apparatus and experimental conditions.

When liquid and solid substances are studied, it is necessary to know the molecular weight and density of the substances studied in order to calculate the CH-group content in the number of groups in a molecule, whereas in order to calculate the percentage weight content of CH_2-groups, it is only necessary to know the

density. The value of the density is not required for the determination of the percentage weight content of CH_2-groups in solution.

The experimental accuracy was found to be ± 1 group for the calculation of the number of groups per molecule, and about 10% for the calculation of the percentage weight content of the groups.

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BRIEF COMMUNICATIONS

LITHIUM TETRA-(p-TOLYL) BORON AS A REAGENT FOR THE QUANTITATIVE DETERMINATION OF SODIUM

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In recent years several articles have appeared which have been devoted to the tetraarylboron salts $MeBAr_4$, where Me is the cation of an alkali metal, while Ar is an aromatic or heterocyclic radical. The interest displayed in these compounds is determined mainly by their capacity to precipitate certain cations in aqueous solutions. Thus, sodium tetraphenyl boron precipitates the cations K^+, Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+ etc. There are more than one hundred papers devoted to the use of sodium tetraphenylboron in analytical chemistry. However, among known salts of this type there are no sodium salts which are sparingly soluble in water, and in which form sodium could be determined quantitatively. According to available results [1], the solubility of $MeBAr_4$ salts in water depends on the nature of the aryl radical in the anion.

Having used a reaction described previously [2] of a magnesium organic compound with sodium borofluoride, we found that during the interaction of p-tolylmagnesium bromide with $NaBF_4$ sodium tetra(p-tolyl) boron which is sparingly soluble in water is formed:

$$NaBF_4 + n = CH_3C_6H_4MgBr \rightarrow NaB(C_6H_4CH_3)_4.$$

Lithium tetra-(p-tolyl) boron, a salt which is readily soluble in water, is obtained from sodium tetra-(p-tolyl) boron by a double exchange reaction with $LiBF_4$ in alcoholic solution:

$$NaB(C_6H_4CH_3)_4 + LiBF_4 \rightarrow LiB(C_6H_4CH_3)_4 + \downarrow NaBF_4.$$

lithium tetra-(p-tolyl) boron forms colorless crystals which are readily soluble in water, alcohol, acetone, and ether; it is insoluble in petroleum ether. An aqueous solution of the lithium salt gradually changes in contact with air. Lithium tetra (p-tolyl) boron in aqueous solutions precipitates Na^+, K^+, Rb^+, Cs^+, etc.

Wittig and Herwig [3] synthesized lithium tetra (p-tolyl) boron from tri (p-tolyl) boron and p-tolyl lithium; the authors do not point out that this salt precipitates sodium ions.

We have used lithium tetra (p-tolyl) boron for the quantitative determination of sodium. A 10-13% solution of lithium tetra (p-tolyl) boron (1.85-2.0 g) in water was prepared; to this was added 2-3 drops of a 3% solution of NaCl before formation of a precipitate, in order to saturate the solution beforehand with sodium tetra (p-tolyl) boron. The solution was then filtered. The reagent prepared in this way was used for sodium determination. To 1 ml of an aqueous solution of NaCl containing 0.0301 g of NaCl was added 3-4 ml of reagent; after 5-10 minutes, the precipitate was transferred to a crucible fitted with a filter, and the rest of the precipitate washed onto the filter crucible by means of reagent solution. The precipitate was washed 4-5 times with 1.5-2 ml lots of reagent solution, after which it was dried at room temperature in a desiccator (under a small vacuum) over P_2O_5. The dry precipitate was then washed free from $LiB(C_6H_4CH_3)_4$ by means of anhydrous ether; it was finally dried in a desiccator (at room temperature) to constant weight.

The experimental results obtained by this method are given in the Table.

Amount of NaCl per ml, g	Weight of $NaB(C_6H_4CH_3)_4$ precipitate		Sodium content of the NaCl, %	
	found	calculated	found	calculated
0.0301	0.2044	0.2052	39.18	39.34
0.0301	0.2050	0.2052	39.30	39.34
0.0301	0.2047	0.2052	39.23	39.34
0.0454	0.3085	0.3094	39.22	39.34

The fact that lithium tetra (p-tolyl) boron precipitates not only Na^+, but also K^+, Rb^+, and Cs^+ will not interfere with its use for determining sodium, since all these cations, apart from sodium, can be quantitatively precipitated beforehand with lithium tetraphenylboron.

An advantage of the method suggested is that it is possible to carry out the work with only small amounts of the tetra (p-tolyl) boron salts, since the sodium tetra (p-tolyl) boron obtained during the analyses is readily reconverted by double decomposition with $LiBF_4$ into $LiB(C_6H_5CH_3)_4$, which can be used for subsequent analyses. Moreover, by using lithium tetra (p-tolyl) boron, it is possible to determine sodium in the presence of lithium, a determination which cannot be carried out by means of the method with uranyl acetate and zinc, since Li^+ forms a sparingly soluble ternary salt with the latter.

Lithium tetra (p-tolyl) boron should not be kept long in air; accordingly, it is best to prepare it immediately prior to use.

Synthesis of Sodium Tetra (p-tolyl) Boron. To 3.5 g of finely ground $NaBF_4$ in a small volume of absolute ether is added a still warm solution of Grignard reagent prepared from 20 g of p-bromotoluene and 2.8 g of magnesium in 70 ml of anhydrous ether (the reaction is carried out in a flask provided with a stirrer and a reflux condenser). The reaction mixture is heated on a water bath for 1.5 hours; after cooling, it is filtered through a No. 1 glass filter. The precipitate on the filter is washed 3-4 times with anhydrous ether. To the ether filtrate consisting of unreacted Grignard reagent is added another 3.5 g of sodium borofluoride, and all the operations repeated. Both precipitates are combined and treated with a small amount of water to remove sodium borofluoride. Sodium tetra (p-tolyl) boron is filtered on a No. 2 glass filter and washed three times with water; it is dried at room temperature in a vacuum desiccator over P_2O_5, for complete removal of moisture. If the precipitate treated with water is kept for a long time on the filter, and air sucked through it, or it is kept in a damp state for a long time in air, then it decomposes. The dried material is dissolved in the minimum amount of acetone. The solution is filtered and absolute ether added to it until no further precipitate is formed. The sodium tetra (p-tolyl) boron is filtered, and washed several times with absolute ether. The yield of the salt is 1.2-1.7 g (10-13% in terms of the p-bromotoluene used).

Found %: C 84.01, 83.89, H 7.29; 7.10; Na 5.99, 5.85 $C_{28}H_{28}BNa$: Calculated %: C 84.41; H 7.09; Na 5.77.

Sodium tetra (p-tolyl) boron in a pure, dry state is fairly stable; it is readily soluble in acetone and ethyl acetate; soluble in alcohol and pyridine; sparingly soluble in water, and insoluble in benzene and absolute water; it is sparingly soluble in wet ether.

The Synthesis of Lithium Tetra (p-Tolyl) Boron. To a solution of 2.5 g of sodium tetra (p-tolyl) boron in the minimum amount of absolute alcohol is added an alcoholic solution of 1.2 g of lithium borofluoride. The precipitate of sodium borofluoride formed is filtered off. The alcohol is removed in a vacuum desiccator over $CaCl_2$. The dry residue is dissolved in absolute ether and filtered free from the undissolved sodium borofluoride taken in excess, and the unreacted sodium tetra (p-tolyl) boron. The ether is removed in a vacuum desiccator. The dry residue is transferred onto a No. 3 or No. 4 glass filter and washed four times with low boiling petroleum ether to free it from ditolyl impurities. Residual petroleum ether is removed in a vacuum desiccator. 2.2 g of lithium tetra (p-tolyl) boron is obtained (85% of theory). This salt is readily soluble in acetone, alcohol, ether, and water; it is insoluble in petroleum ether. Lithium tetra (p-tolyl) boron in the solid state

and in solution does not keep under ordinary conditions; the salt content of its solutions decreases with time; after several hours standing in air, an aqueous solution of $LiB(C_6H_4CH_3)_4$ will no longer give a precipitate with a solution of NaCl.

Analysis of lithium tetra (p-tolyl) boron with the object of determining its lithium content is carried out as follows: an aliquot of the salt is decomposed with 0.1 N HCl. After some time, excess acid is back titrated with alkali.

Found % Li 7.82. $C_{28}H_{28}BLi$: Calculated %: Li 1.81.

The lithium tetra (p-tolyl) boron formed in this way, on dissolving it in water, gives slightly turbid solutions; the solution is carefully filtered before using it for determining sodium.

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THE EXACT DEFINITION OF PEAK POTENTIAL IN OSCILLOGRAPHIC POLAROGRAPHY

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Analysis of solutions by the method of oscillographic polarography reduces to measurement of the potential and the peak height of the diffusion current. The peak potential depends on the nature of the ion studied, while the height is proportional to its concentration. However, in addition to the electrochemical reactions which take place on the electrode, charging of the electrical double layer occurs. The current which corresponds to this process is proportional to the rate of change of potential and reaches a considerable value. The presence in the electrolysis cell of several substances which participate in the electrochemical reaction, also complicates determination by the method of oscillographic polarography. Usually, to the diffusion current (i_d) of the test ion are added other currents (i_b), so that the total current in the electrolysis cell circuit is determined by their sum [1, 2]:

$$i = i_d + i_b. \tag{1}$$

At the point where the diffusion current passes through its maximum, $di_d/dE = 0$ (E is the electrode potential). Differentiation of (1) at the peak gives

$$di/dE = di_b/dE. \tag{2}$$

Accordingly, the method which has been in use previously (Fig. 1a) for measurement, in which the peak potentials of the total and diffusion current are identified with each other, should be replaced by a more refined method, the principle of which is shown in Fig. 1b. Here the peak potential is defined as the point at which the curves for the total current and for the supporting electrolyte have the same slope. If this technique is not adopted then

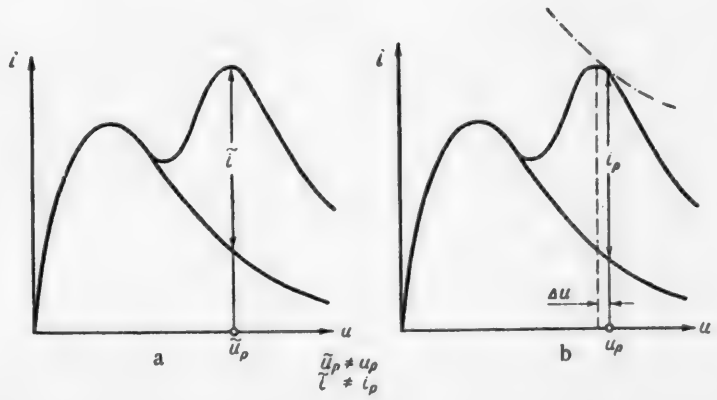

Fig. 1

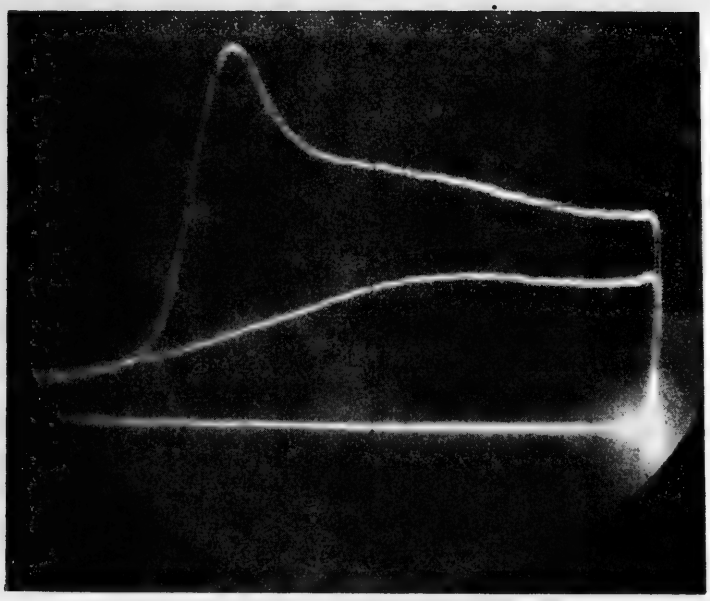

Fig. 2. 20 γ Cd^{2+}/ml in 1 M KCl, α 8.5 volt/second, t = 25°. Dropping mercury electrode, anode polarization with pre-electrolysis.

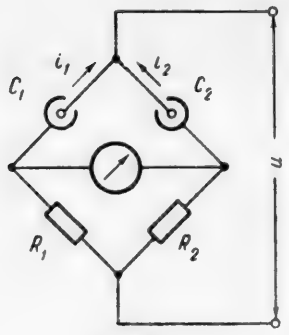

Fig. 3.

has not been established previously.

there will be an error not only in the value of the potential of the maximum, but also in the value of the current which will not be a maximum. The error in the value of the potential is often greater than 10 millivolts in practice, while the rate of change of potential a and the concentration C of the ion participating in the electrochemical reaction will affect its value. The capacity current which makes up part of i_b increases in proportion to a. The curvature of the peak increases with concentration C. Accordingly, the error increases on increasing α and decreasing C. This explains the potential shift on changing the concentration. While the ohmic drop in potential, on increasing the concentration, always shifts the peak towards the higher voltage applied to the cell, the direction of the shift caused by the supporting electrolyte current has not been established previously.

In order to determine the true peak potential on an oscillogram, the curves for total current and supporting electrolyte current are combined. The curves for the test solution, and for the electrolyte serving as the supporting electrolyte, are photographed by successive exposures on one frame of film. In Fig. 2 are shown the anode wave for Cd in 1 N KCl, the supporting electrolyte current, and the zero line. Such a combined photograph makes it possible to carry out a rapid evaluation of the true values of the current and the potential. In the example given, the apparent shift in peak potential was + 10 millivolts. Subtraction of the supporting electrolyte current from the total current on the oscillogram can be substituted by carrying out the subtraction in the electric circuit of the polarograph itself. Electrical circuits for subtracting currents are well known. It should be pointed out that a bridge setup in its original form is not applicable for subtraction of polarographic currents. In actual fact, let U be the potential applied to the bridge, R_1 and R_2 the load resistances, and C_1 and C_2 the electrolyzers containing test solution and the electrolyte used as supporting electrolyte (Fig. 3). Then the potential drop across the electrolyzers C_1 and C_2 will be, respectively:

$$U_1 = U - i_1 R_1; \quad U_2 = U - i_2 R_2.$$

But, since for a given bridge, R_2/R_1 = const, while i_1/i_2 for different solutions can change arbitrarily, then

$i_1/i_2 \neq R_2/R_1$ and $U_1 \neq U_2$. Thus, at the very same moment, different potentials will correspond to the minuend and the subtrahend. This destroys the elementary rule for the subtracting of functions, and in this connection will affect the correctness of the result obtained.

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DETERMINATION OF ALUMINUM IN SOLUTIONS CONTAINING FLUORIDE IONS BY MEANS OF 8-HYDROXYQUINOLINE

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Aluminum ions form with fluoride ions complex ions which dissociate only very slightly; of these ions the most stable are AlF^{2+} ($K_{AlF^{2+}} = 5 \times 10^{-6}$) and AlF_2^+ ($K_{AlF^{2+}} = 8.7 \times 10^{-10}$). Naturally, therefore, ordinary reagents will not react with aluminum ions if fluoride ions are present in solution.

Table 1 contains some results which illustrate the effect of the amount of fluoride ions in solution on the degree of precipitation of aluminum by 8-hydroxyquinoline. In all cases precipitation was carried out under ordinary conditions, in a medium of an acetate buffer solution. The volume was 50 ml in each case. Fluoride ions were introduced as NH_4F.

As is evident from the table, precipitation of aluminum hydroxyquinolate is incomplete at a molar ratio of F:Al as low as 0.25. At a ratio of F:Al = 1, i.e., when all the aluminum in solution is complexed as AlF^{2+}, no precipitate is formed at all. Usually, the test solution is evaporated several times with excess H_2SO_4 or $HClO_4$ until all fluoride ions have been removed; this operation, however, takes up too much time. Attempts have been made to determine aluminum as its 8-hydroxyquinolate in the presence of boric acid which reacts with fluoride ions to form fluoroborates. Unfortunately, the latter are formed in acid solution; under the low

TABLE 1

Effect of Fluoride Ion Concentration on the Degree of Precipitation of Aluminum by 8-Hydroxyquinoline

Molar ratio F:Al	Al	
	taken	found
0.0	0.0286	0.0285
0.25	0.0286	0.0255
0.5	0.0286	0.0191
1.0	0.0286	0.0000

acidity conditions which are necessary for precipitation of aluminum hydroxyquinolate, the fluoroborates hydrolyze. Multivalent cations (Fe^{3+}, Ti^{4+}, ZrO^{2+} etc.) are not suitable for complexing the fluoride ions in the case under discussion, since most of these cations are precipitated by the 8-hydroxyquinoline together with the aluminum.

TABLE 2

Determination of Aluminum by Means of 8-Hydroxyquinoline in the Presence of Fluoride and Beryllium Ions (0.0286 g Al taken(F:Al = 1:1)

Be : Al	Al found, g
0.5	0.0281
0.5	0.0282
1.0	0.0286
1.0	0.0286

Beryllium forms very stable complex compounds with fluoride ions ($K_{BeF^+} = 2 \times 10^{-6}$), while at the same time, under the conditions used for precipitating aluminum with 8-hydroxyquinoline (acetate buffer), the beryllium is not precipitated. This led us to the idea of using beryllium ions for complexing the fluoride ions during precipitation of aluminum in the presence of fluoride.

As the result in Table 2 show, beryllium ions enhance the capacity of aluminum to be precipitated with 8-hydroxyquinoline. Even at a molar ratio of Be:Al = 0.5, the effect is very considerable (when lower relative amounts of beryllium are used,the results for aluminum are strongly depressed). However, completely reliable results can be obtained on using a molar ratio of Be:Al = 1. Obviously, the following reaction occurs in solution during the precipitation process:

$$AlF^{2+} + 3Ox + Be^{2+} \rightarrow \downarrow Al|Ox|_3 + BeF^+.$$

Larger amounts of beryllium in solution do not interfere with aluminum determinations.

We suggest that the method recommended by us for the determination of aluminum in solutions containing fluorides can be used in practice under conditions which enable the beryllium to be regenerated from the working solutions; this does not present any great difficulty.

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DETERMINATION OF ALKALI METALS BY A SPECTROGRAPHIC METHOD

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A method was published earlier [1] for spectrographic analysis based on lines located in different parts of the spectrum. As an example, a description was given of the spectrographic determination of the ratio of the concentration of sodium to that of potassium on the basis of the lines Na 3302.3 and K 4044.1. It was assumed that the total sodium and potassium was known and had been determined by a chemical method. By solving the system of equations

$$c_{Na} + c_K = A; \quad c_{Na}/c_K = B,$$

where A is the value found by the chemical method, and B is the value found by the spectrographic method, it is easy to calculate the concentrations of sodium and potassium.

The present work describes a spectrographic method for the determination of the alkali metals in solution, when their sum is not known. The ratio c_{NA}/c_K was determined, as in the previous article, by exciting the spectra in an arc struck between copper electrodes soaked with the test solution, and using the lines Cu 3290.5 and Cu 4022.7.

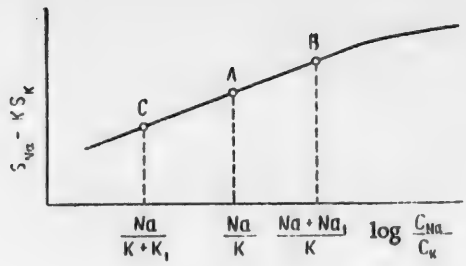
Having constructed a curve within the coordinates $\left(S_{Na} - kS_K; \frac{c_{Na}}{c_K}\right)$ according to a formula obtained previously [1]: $S_{Na} - kS_K = \gamma_{Na} b \log \frac{c_{Na}}{c_K} + \gamma_{Na} \log a$ where the coefficient $k = \frac{\gamma_{Na}\, r}{\gamma_K}$ depends on the contrast factors for the lines Na 3302.3 and K 4044.1, and on the heterogeneity coefficient of the photographic plate r, it is possible to find the ratio of the concentrations c_{Na}/c_K. Let us assume that on the curve for a given solution the coordinates indicated correspond to point A. If a solution of a pure sodium salt or a pure potassium salt is added to the test solution, then obviously the ratio of the concentrations of these metals will change, and points B or C on the curve will correspond to the solution obtained. Knowing the amounts of sodium or potassium salt added, it is easy to calculate their amounts in the test solution. The problem reduces to taking two photographs of the spectra in order to determine the ratio of the concentrations of the alkali elements in the original solution, and in the solution obtained after adding a known weight of one of the metals to the original solution.

Let a known volume of test solution contain (Na) g of sodium and (K) g of potassium. Then the ratio of their concentrations will be

$$\frac{Na}{K} = a. \tag{1}$$

If, to this solution is added a standard solution containing a known weight of sodium (Na_1) g, then, obviously, the ratio of the concentrations will change to:

$$\frac{(Na + Na_1)}{K} = b \tag{2}$$



Dividing equation (2) by equation (1), we get $\frac{(Na + Na_1)}{Na} = \frac{b}{a}$, from which

$$Na = \frac{Na_1}{(b/a-1)}. \quad (3)$$

By substituting the latter in equation (1), we get

$$K = Na_1/(b-a). \quad (4)$$

If a standard solution of potassium is added to the test solution, then, in a similar way

$$Na/(K+K_1) = d. \quad (5)$$

Dividing equation (1) by (5), we get $(K + K_1)/K = \frac{a}{d}$, from which

$$K = \frac{K_1}{(a/d-1)}. \quad (6)$$

By substituting the value of K in equation (1) we get $Na = \frac{aK_1}{(a/d-1)}$.

Having determined the ratio of the concentrations a and b or d, in solution, and knowing the amount of added sodium Na_1 or K_1, it is easy to find the amounts of these elements in the test solution by using either (3) and (4) or (6) and (7) respectively.

Results for the Determination of Alkali Metals in Solution

Actual content, g/ml		Amount found, g/ml		Relative error, %	
Na	K	Na	K	Na	K
0,01045	0,01229	0,01062	0,01252	+1,5	+1,9
0,00925	0,01388	0,00950	0,01372	+2,7	−1,2
0,00833	0,01386	0,00820	0,01408	−1,6	+1,6
0,00635	0,01584	0,00644	0,01563	+1,4	−1,3
0,00565	0,01632	0,00540	0,01654	−2,6	+1,3
0,00333	0,01667	0,00346	0,01637	+3,9	−2,9
0,00278	0,01940	0,00288	0,01931	+3,6	−1,6
0,00247	0,01971	0,00239	0,01995	−3,2	+0,5
0,00222	0,01996	0,00230	0,02027	+3,6	+1,2
0,00182	0,01818	0,00189	0,01849	+3,8	+1,7
0,00159	0,02059	0,00154	0,02043	−3,1	−0,8
0,00148	0,01848	0,00155	0,01858	+4,1	+0,5
0,00131	0,02087	0,00126	0,02071	−3,8	−1,2
Mean arithmetical error				3,0	1,3

In order to check the method we analyzed specially prepared, approximately 5% mixed solutions of sodium and potassium sulfates, and also a 5% solution of potassium sulfate. In order to determine the ratio of concentrations a, 0.5 ml of the standard solution was added to each ml of test solution. The ratios of the concentrations a and d were determined by means of the method described previously [1], after which the content of the alkali metals was calculated by means of (6) and (7).

The accuracy for determination of sodium is about 4%, while for potassium it is about 2% (relative) see Table.

It should be pointed out that the comparatively high accuracy obtained for the spectrographic determination of these elements, despite the large distance separating the analytical lines, is determined in this particular

instance by the identity of the analytical lines Na 3302.3 and K 4044.1, and also by the similarity between the physical and physicochemical properties of sodium and potassium salts.

Third components do not affect the experimental results [2].

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A NEW LUMINESCENT METHOD OF MICROCHEMICAL ANALYSIS (CRYSTALLOPHOSPHOR)

COMMUNICATION 2. DETECTION OF TIN

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Most of the qualitative microchemical reactions used for the detection of tin are based on oxidation–reduction reactions. Detection of tin in mixtures containing Fe, Ce, Sb, Bi, As, Hg, etc., is very difficult. At the same time tin can readily be detected by means of potassium iodide on filter paper on the basis of the formation of a crystallophosphor [1].

During a study of qualitative reactions for Tl^+ we noticed that tin ions interfered; the latter, on carrying out the reaction for thallium, produced a bright yellow luminescence [2, 3]. Solutions of sodium and potassium chloride, bromide, and iodide were tested as reagents for tin. Potassium iodide proved to be the best; potassium iodide gives with solutions of tin salts a bright yellow luminescence, the latter develops after drying out the reaction products and illuminating them with an ultraviolet beam. It is of interest to note that the radiation of potassium iodide activated by tin, differs from the radiation of potassium iodide activated by thallium, not only in its color, but also in that the color of the radiation does not change with concentration; only the intensity changes.

In order to establish the sensitivity of the reaction we used a solution of $SnCl_2$ containing 2.33 mg/ml of Sn^{2+}, and this solution diluted 10, 100, and 1000 times. A bright yellow luminescence was observed with all these solutions, the intensity of the luminescence decreasing with decreasing tin concentration. On diluting further the reaction became indistinct. Thus the limit of identification of tin by this reaction is 0.02 μg of Sn at a limiting dilution of $1 : 5 \times 10^5$. The sensitivity can be increased by using a piece of unglazed porcelain plate instead of paper. When unglazed porcelain is used the limit of identification becomes 0.0002 μg at a limiting dilution of $1: 5 \times 10^6$. The order in which the reaction is carried out has considerable effect on the reaction sensitivity.

Experimental Procedure. A drop of test solution with a volume of 0.001 ml (the diameter of the spot obtained on the filter paper is 3 mm) is placed on a piece of filter paper by touching the paper with a capillary tube containing test solution; some potassium iodide solution is then superimposed on the center of the spot by means of a capillary tube. The potassium iodide solution is allowed to flow out of the capillary so that it covers the whole area of the spot given by the test solution. The drop is dried out and then examined under ultraviolet light. Should a weak luminescence appear the paper is dried further, after which the luminescence should strengthen. The paper should not be overheated; otherwise the potassium iodide will decompose, and the liberated iodine will adsorb the ultraviolet rays and strongly weaken the luminescence, almost to the point of extinguishing it completely. When appreciable amounts of tin are present, an intense yellow luminescence appears at the center of the spot; this is surrounded by a ring of iodine colored red. When the amount of tin is small, the luminescence which is still clearly observed is more diffuse and is redder. When the potassium iodide is placed on the paper before the test solution, a luminescent ring is obtained with a dark center, as a rule.

As indicated previously [1], on carrying out luminescent reactions in which crystallophosphors are formed, interfering elements of two types have been observed. Elements of the first type are those which form similar

crystallophosphors (in this instance, these elements are Hg_2^{2+}, Tl^+, and, to some extent, Ag^+ and Cu^+). Elements of the second type are those which extinguish the luminescence of the crystallophosphor (in this instance, these elements are Hg^{2+}, Sb^{3+}, As^+, Ag^+, Pb^{2+}, Fe^{3+}, Cu^{2+}). Zinc, cobalt, nickel, germanium, zirconium, gallium, indium, titanium, cadmium, manganese, tungsten, molybdenum, and divalent iron do not interfere with detection of tin.

When Hg_2^{2+} and Hg^{2+} are present the following procedure is adopted: a small drop of potassium iodide solution is placed on the filter paper, this is followed by a drop of the test solution; a further drop of potassium iodide is then added until the mercury iodides have dissolved. When divalent mercury is present, the precipitate dissolves completely and the complex compound formed $K_2[HgI_4]$ does not interfere with detection of tin right up to the point where the solution is saturated with mercury. When univalent mercury is present, on addition of excess potassium iodide metallic mercury is formed, while the precipitate of mercurous iodide is converted into mercuric iodide which is subsequently converted into the complex $[HgI_4]^{2-}$. The metallic mercury formed does not interfere with detection of tin.

It should be pointed out that Hg_2I_2 also exhibits its own characteristic luminescence with a reddish color, but under the conditions used for detecting tin, this reaction is not given so that the mercury does not interfere with detection of tin. Under the conditions used for the reaction for tin, thallium exhibits its own luminescence [2] the color of which depends on concentration; on mixing with the luminescence arising from the presence of tin, the luminescence of thallium acquires almost a pure white color. When the amount of thallium is small, interference on its part can be suppressed by observing the luminescence which arises in ultraviolet with $\lambda = 365$ mμ; at this wavelength the thallium radiation is strongly weakened, while the color of the luminescence arising from the presence of tin changes from a golden-yellow to a greenish-yellow.

When large amounts of thallium are present it is best to remove the tin, even if only half of it, by extraction and then carry out the reaction for tin on the extract.

Sb^{3+}, Bi^{3+}, As^{3+}, Ag^+ and Pb^{2+} ions form strongly absorbing precipitates of iodide. Silver iodide is itself capable of giving a luminescence, but under the conditions used for the reaction for tin, it does not luminesce and does not interfere. Interference from trivalent iron and divalent copper reduces mainly to liberation of elemental iodine. The permissible limiting ratios for the interfering elements during the detection of tin in a drop of 0.001 ml (0.002 μg of Sn^{2+}) are as follows:

$Sn^{2+} : Sb^{3+} = 1 : 100\,000$	$Sn^{2+} : Pb^{2+} = 1 : 10\,000$
$Sn^{2+} : Bi^{3+} = 1 : 100\,000$	$Sn^{2+} : Fe^{3+} = 1 : 1\,000$
$Sn^{2+} : As^{3+} = 1 : 10\,000$	$Sn^{2+} : Cu^{2+} = 1 : 1\,000$
$Sn^{2+} : Ag^+ = 1 : 30\,000$	

Detection of Tin in Sulfide Rocks. A grain of sulfide rock is placed on a watch glass and treated with concentrated hydrochloric acid, or a mixture of hydrochloric and nitric acids; complete dissolution of the sample is not essential. The solution, which is usually turbid, is transferred onto filter paper by means of a capillary. The procedure given above is then followed; quite satisfactory and distinct results are obtained.

Detection of Tin in Alloys can be carried out in several ways:

a) a grain of alloy is treated on a watch glass with hydrochloric acid and the solution transferred onto filter paper, tin is detected on the latter by the method described above;

b) a very small drop of acid is placed directly on the surface of the alloy and allowed to stand there for some time. So that the drop does not dry out, the spot at which the reaction is carried out is kept moist by breathing on it. The solution is finally transferred onto paper and detection of tin carried out.

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DETERMINATION OF MOLYBDENUM IN ALLOYS BY MEANS OF 8-MERCAPTOQUINOLINE

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8-Mercaptoquinoline (thiooxine) is the sulfur-containing analog of 8-hydroxyquinoline. It has been studied as an analytical reagent by Yu. A. Bankovskii [1, 2].

The selectivity of the reagent in a number of cases makes it possible to determine traces of certain elements in the presence of predominant amounts of other elements, e.g., traces of copper in the presence of large amounts of iron [2].

The problem confronting us was to develop a photometric method for the determination of molybdenum with 8-mercaptoquinoline in multicomponent alloys. 8-Mercaptoquinoline forms a green intercomplex salt with molybdenum which is readily extracted from acid solutions. The composition of the compound has been established by Bankovskii [3] and is expressed by the formula $MoO_2(C_9H_6NS) \cdot H_2O$.

We have checked the method used by Yu. A. Bankovskii [3].

In our experiments the limit of identification proved to be 0.2 γ of Mo at a limiting dilution of 1 : 1,000,000.

The color obtained on extracting 5 γ of Mo from a solution containing 2.5 ml of 2.5 N HCl, 2.5 ml of 10% ascorbic acid, 1 ml of 5% thiooxine hydrochloride (25 ml of concentrated HCl and 75 ml of water), and 1 ml of toluene is identical with the color of 5 γ of Mo (standard solution) extracted under similar conditions, but not containing ascorbic acid; thus, ascorbic acid (in the amount indicated) does not affect the color given by molybdenum with 8-mercaptoquinoline. This means that it is possible to determine molybdenum in the presence of iron.

On extracting 5 γ of Mo in the presence of 2 ml of a saturated solution of oxalic acid* and 2.5 ml of 10% ascorbic acid, there is observed a considerable weakening of the color in comparison with the color obtained when 5 γ of Mo is extracted from a solution not containing oxalic acid and ascorbic acid. During extraction of 5 γ of Mo from 2.5 N HCl in the presence of 2 ml of an 8% solution of thiourea, a pale green color develops, which differs strongly in color from the color of the extract of 5 γ of Mo from a standard solution not containing thiourea. Thus, only ascorbic acid can be used during the extraction of molybdenum in the presence of iron.

In order to determine molybdenum in the presence of tungsten we tested the following: oxalic, succinic, and phosphoric acids. The two latter acids proved to be the most suitable.

Results of the photometric determination of molybdenum with 8-mercaptoquinoline in the presence of other elements are given in Table 1.

The effect of the concentration of HCl and H_2SO_4 on the percentage extraction of 10 γ of Mo with toluene (2 ml) was studied. The amount of reagent in the volume of solution used was not changed during the experiments.

*Bankovskii recommends using 10 ml of a saturated solution of oxalic acid and 5 ml of 10% ascorbic acid.

TABLE 1

Determination of 1 γ of Mo in the Presence of Other Elements at pH 1

Element present, γ	Ratio Mo:Me, γ	Element present, γ	Ratio Mo:Me, γ
Co^{II}	1 : 3	V^{V}	1 : 100
Cr^{III}	1 : 10	Ni^{II}	1 : 150
W^{VI}*	1 : 10	T^{IV}	1 : 750
Fe^{II}**	1 : 55	Al^{III}	1 : 1800

*In the presence of 0.01 ml of concentrated H_3PO_4.
**In the presence of 2 ml of 10% ascorbic acid.

On extraction of the molybdenum, after shaking the layers up for 3 minutes, the amount of molybdenum remaining in the lower layer of the solution was determined (after destroying the organic reagent).

The experiments (Fig. 1) showed that when the medium has an acidity of 1-10 N HCl, the molybdenum is completely extracted. No experiments were carried out at concentrations in excess of 10 N HCl. Extraction of molybdenum from the sulfuric acid solutions gives satisfactory results starting at an acidity of the solution of 3 N H_2SO_4 (Fig. 1).

TABLE 2

Effect of Time on the Color of the Complex (5 γ Mo, SF-4)

Times, minutes	Optical density, D
–	0.265
15	0.263
30	0.258
45	0.257
60	0.257
75	0.256
90	0.254

The molybdenum was extracted in solution with 2 ml of toluene by shaking for 3 minutes; extraction was carried out in glass cylinders (capacity 30 ml, diameter 14 mm). The green color of the extract containing 5 γ Mo is fairly stable (Table 2).

Solutions containing from 1 to 10 γ of Mo in 1 ml conform to Beer's law.

The method for determining molybdenum with 8-mercaptoquinoline was developed for the purpose of analyzing multicomponent alloys. When the alloys contain tungsten, the latter is kept in solution by adding concentrated phosphoric acid.

An aliquot of chrome-nickel or titanium alloys (0.01 g) is weighed out on a VT-20 torsion balance made by the "Texstil'pribor" factory (scale division 0.02 mg), and provided with two lenses. One of the lenses moves together with the balance needle—the weight indicator. Weighing takes two minutes.

Results of the determination of molybdenum with 8-mercaptoquinoline are given in Tables 3 and 4.

During analysis of alloys containing tungsten it should be borne in mind that the solution obtained can be kept without change for 8 hours, if phosphoric acid is added to keep the tungsten in solution. At the end of this period tungstic acid is precipitated.

Experimental Procedure. 0.01 g of chrome-nickel alloy weighed out on a VT-20 microbalance is dissolved in 5 ml of concentrated HCl contained in a small beaker. If the turning does not dissolved completely, another 2 ml of N HCl is added. When it has dissolved, 5 drops of concentrated HNO_3 is added and the solution heated.

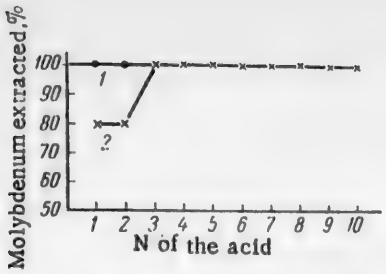

Fig. 1. Relation between extraction of 10 γ Mo and acid concentration: 1) HCl; 2) H_2SO_4.

1.5 ml of concentrated H_2SO_4 is added and the solution evaporated to the appearance of white fumes of sulfuric acid (evaporation is repeated three times until the odor of nitric acid has completely disappeared). On cooling, if any tungsten should be present, 1 ml of concentrated H_3PO_4 is added, followed by 1.5 ml of water and the contents of the beaker heated on an electric hotplate, on a thick sheet of asbestos, until the salts have dissolved completely (overheating should be avoided so as to prevent precipitation of tungstic acid).

The clear solution is transferred to a 100 ml standard flask. 1-3 ml of this solution is pipetted into a graduated colorimeter tube with a capacity of 30 ml and a diameter of 14 mm in order to determine the molybdenum. The reagents are then added in the following order: 2 ml of 2.5 N HCl, 2 ml of water, 1 ml of 10% ascorbic acid* and 1 ml of 5% 8-mercaptoquinoline solution (5 g of reagent is dissolved in 25 ml of concentrated HCl and 75 ml of water). The contents of the tube are then shaken up and 2 ml of toluene added. The molybdenum is extracted by careful shaking for 3 minutes. The phases are allowed to separate. When the method of standard series is used, the colored solution is compared with a series of standard solutions prepared in the same way as the test solution.

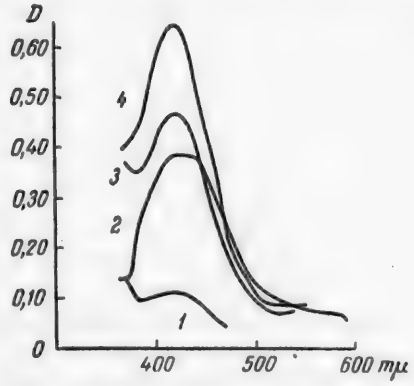

Fig. 2. Light absorption curves for molybdenum with 8-mercaptoquinoline: 1) 5 γ; 2) 10 γ; 3) 20 γ; 4) 30 γ.

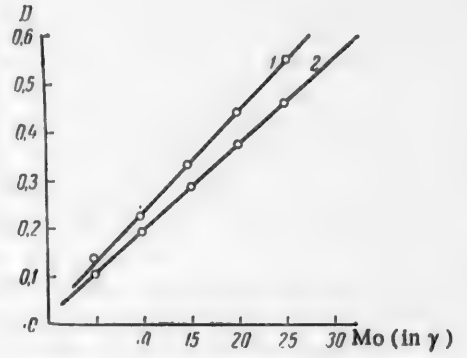

Fig. 3. Calibration curves for the determination of molybdenum in alloys: 1) in chrome-nickel alloys; 2) in titanium alloys.

TABLE 3

Determination of Molybdenum with 8-Mercaptoquinoline in Nickel Based Alloys (aliquot of alloys 0.01 g)

Mo taken,* γ in the aliquot	Mo found, γ	Mo content, %	W content of the alloy, %	Mo found, %	Error, %
12,0	12,20	12,00	—	12,20	1,75
4,90	5,00	4,90	—	5,00	+0,01
3,60	3,60	3,60	—	3,60	—
2,45	2,50	2,45	—	2,50	+0,05
1,20	1,20	1,20	—	1,20	—
0,60	0,60	0,60	—	0,60	—
5,20	5,20	5,20	10,0	5,20	—
3,50	3,30	3,50	10,0	3,30	0,2
2,20	2,20	2,20	12,0	2,20	—
0,90	0,80	0,90	8,0	0,80	0,1

*The molybdenum content of the alloys was established by the thiocyanate method using thiourea.

*When tungsten is present, 1 ml of concentrated H_3PO_4 is added. In this case ascorbic acid should not be added.

TABLE 4

Determination of Molybdenum in Titanium Alloys Containing 1.5% Chromium (aliquot of alloy 0.01 g)

Mo taken, γ in the aliquot	Mo found, γ	Mo content, %	W added to the alloy, %	Mo found, %	Error, %
8,20	8,40	8,20	—	8,40	+0,2
6,30	6,40	6,30	—	6,40	+0,1
4,20	4,22	4,20	—	4,22	+0,02
2,60	2,60	2,60	—	2,60	—
0,65	0,65	0,65	—	0,65	—
4,50	4,50	4,50	20,0	4,50	—
4,50	4,50	4,50	15,0	4,50	—
4,50	4,50	4,50	10,0	4,50	—
4,50	4,50	4,50	5,0	4,50	—
4,50	4,50	4,50	3,0	4,50	—

For spectrophotometric determination, it is more convenient to extract from 5 ml of test solution, with subsequent addition of all the reagents and 5 ml of toluene. 4.0 ml is pipetted from the extract and filtered through a microfunnel containing a small plug of cotton wool. The filtered liquid is poured into a quartz cuvette (10mm). The null solution is placed in the parallel cuvette; the null solution is prepared under similar conditions, using all the reagents, but excluding molybdenum. The optical density is measured at 420 mμ (Fig. 2). The molybdenum content is determined by means of a calibration curve constructed on the basis of solutions of the chrome-nickel alloy "nimonik" to which known amounts of molybdenum are added (Fig. 3).

For determination of molybdenum in alloys based on titanium, 0.01 g of sample weighed out on a VT-20 torsion microbalance is dissolved in 5 ml of concentrated H_2SO_4 contained in a 50 ml beaker; 7 drops of concentrated HNO_3 is added (when this amount of HNO_3 is used the blue color of the solution disappears completely). The clear, bright solution is evaporated three times to the appearance of sulfuric acid fumes. On cooling, 1.5 ml of concentrated H_3PO_4 is added (for tungsten contents up to 5%). When the tungsten content exceeds 5%, 1.25 ml of a 5% solution of succinic acid is added. The clear solution is transferred to a 100 ml standard flask. The procedure outlined for the analysis of chrome-nickel alloys is then followed. The determination can be carried out visually using the standard series method, or spectrophotometrically (Fig. 2) from a 5 ml aliquot of the solution.

I should like to thank Yu. A. Bankovskii and N. A. Uedinova for donating reagent.

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SPECTROGRAPHIC ANALYSIS BY THE EVAPORATION METHOD

COMMUNICATION 8. ANALYSIS OF ZIRCONIUM*

A. I. Zaidel', L. V. Lipis, and K. I. Petrov**

It is difficult to separate out the weak lines of the spectra of impurities contained in small amounts in zirconium against the background of the multilinear spectrum of zirconium itself. This difficulty can be overcome either by using spectrographs with a high dispersion (this technique has been used by a number of American workers [1, 2]) or by separating the zirconium from the impurities, on the basis of differences in the volatility of the oxides (methods of fractional distillation in a d.c., arc [3]), or on the basis of differences in their chemical properties (spectrochemical methods [4-6]). Of the methods based on fractional distillation the most efficient is the evaporation method [7-10].

Of undoubted promise for the determination of impurities in zirconium dioxide is discharge in a hollow cathode [13]. Its insignificant vapor pressure at comparatively high temperatures [11, 12] has made it possible to have confidence in the successful application of the evaporation method to the determination of impurities in zirconium dioxide. Accordingly, a technique has been developed with precisely this compound in view; other zirconium compounds (nitrate, hydroxychloride, etc.) and also zirconium metal, on calcining in air at 700-800° are readily converted into zirconium dioxide. The conversion of zirconium metal and zirconium compounds into the dioxide leads to an easy solution of the problem of standards, since synthetic standards based on zirconium dioxide are prepared very easily.

The success of the evaporation method depends on the correct choice of the temperatures for heating the samples; the temperature chosen should ensure complete or reproducible separation of the impurities to be determined from the main component of the test sample. The optimum temperature for heating zirconium dioxide at normal pressure in air, and even at reduced pressure is 2000-2100°. At such a temperature the impurities to be determined: B, Bi, Cd, Cr, Fe, K, Na, Li, Ni, Mn, Pb, Sb, Sn, and Si are evaporated off almost completely in 1-1.5 minutes, while Al and Mg are removed to a considerable extent. Evaporation of zirconium dioxide becomes appreciable at temperatures in excess of 2100°. The extent to which some impurities are removed from zirconium dioxide by evaporation was subsequently checked by means of radioactive indicators [9].

The conditions used for spectrographic analysis of the condensate (the parameters of the spark generator, the size of the interelectrode gap, etc.) do not differ from those described in previous communications: L = 0.15 μH, C = 0.01 μF, d = 2 mm. Comparison of the results obtained on evaporating off impurities from ZrO_2 in air and at reduced pressure (about 0.01 mm Hg), showed that with respect to the sensitivity and reproducibility of the determination of all the elements, with the exception of Bi, Cd, Pb, Sb, and Sn, the vacuum variant of the evaporation method is the more advantageous (results for some of the elements are given in Table 1).

During evaporation of the impurities under reduced pressure there are formed even and stable layers of condensate, thanks to which the material passes more efficiently into the discharge zone. A higher condensation coefficient is observed on evaporating the impurities under reduced pressure (the exceptions are Bi, Cd, and Pb for which the condensation coefficient in a vacuum is lowered as a result of a reverse, uncontrolled evaporation of the impurities back from the electrode-receiver) [9].

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*For Communication 7, see J. Anal. Chem. 14, 135 (1959).

**The work described here was carried out in 1952-53.

TABLE 1

Blackening of the Analytical Lines during Evaporation of Impurities at Normal Pressure and at Reduced Pressure

Evaporation conditions	Blackening					
	Al	B	Fe	Mg	Li	Pb
At normal pressure	0.43 ± 0.08	0.89 ± 0.08	0.82 ± 0.07	1.55 ± 0.10	0.91 ± 0.08	0.73 ± 0.07
Under vacuum	0.65 ± 0.07	1.09 ± 0.06	1.02 ± 0.06	1.82 ± 0.10	1.03 ± 0.07	0.29 ± 0.14

Note: 1) The sample of ZrO_2 contained 1×10^{-4}% each of B and Li, 1×10^{-2}% each of Al, Fe, Mg, and Pb. 2) Each blackening value is the mean of 20 measurements. 3) The analytical lines given in Table 2 were used.

TABLE 2

Analytical Pairs of Lines

Analytical line A	Reference line, A	Concentration ranges determined, %
Al I 3082,2	Ga I, 2874,2	$1 \cdot 10^{-3}$—$3 \cdot 10^{-2}$
Si I 2881,6	2874,2	$1 \cdot 10^{-4}$—$1 \cdot 10^{-1}$
Mg I 2852,1	2874,2	$1 \cdot 10^{-4}$—$3 \cdot 10^{-2}$
Bi I 3067,7	2874,2	$1 \cdot 10^{-5}$—$1 \cdot 10^{-3}$
Sn I 2840,0	2874,2	$1 \cdot 10^{-4}$—$1 \cdot 10^{-2}$
Pb I 2833,1	2874,2	$1 \cdot 10^{-4}$—$1 \cdot 10^{-2}$
B I 2496,8	Ga I 2500,2	$1 \cdot 10^{-5}$—$3 \cdot 10^{-4}$
Cd I 2288,0	2500,2	$1 \cdot 10^{-5}$—$3 \cdot 10^{-4}$
Sb I 2598,1	2500,2	$1 \cdot 10^{-4}$—$3 \cdot 10^{-3}$
Fe II 2410,5	Co II 2363,3	$1 \cdot 10^{-3}$—$1 \cdot 10^{-1}$
Fe II 2382,0	2363,3	$1 \cdot 10^{-4}$—$1 \cdot 10^{-2}$
Ni II 2316,0	2363,3	$3 \cdot 10^{-4}$—$3 \cdot 10^{-2}$
Mn II 2593,7	Co II 2580,3	$3 \cdot 10^{-5}$—$3 \cdot 10^{-3}$
Cr II 2843,2	2580,3	$1 \cdot 10^{-4}$—$3 \cdot 10^{-2}$
Li I 6707,8	Analysis was carried out on the basis of the absolute blackening.	$1 \cdot 10^{-5}$—$3 \cdot 10^{-4}$
Na I 5889,9		$3 \cdot 10^{-4}$—$1 \cdot 10^{-2}$
K I 7664,9		$1 \cdot 10^{-3}$—$3 \cdot 10^{-2}$

TABLE 3

Comparison of Results of Determination by Chemical and Spectrographic Methods

Sample No.	Fe, %		Si, %		Ni, %	
	spectrographic	chemical	spectrographic	chemical	spectrographic	chemical
1	$5,3 \cdot 10^{-2}$	$4,8 \cdot 10^{-2}$	$3,5 \cdot 10^{-2}$	$3,3 \cdot 10^{-2}$	$1,0 \cdot 10^{-3}$	$1,0 \cdot 10^{-3}$
2	$1,5 \cdot 10^{-2}$	$1,4 \cdot 10^{-2}$	$2,0 \cdot 10^{-2}$	$2,1 \cdot 10^{-2}$	$9,0 \cdot 10^{-4}$	$1,0 \cdot 10^{-3}$
3	$7,0 \cdot 10^{-2}$	$6,8 \cdot 10^{-2}$	$2,2 \cdot 10^{-2}$	$2,5 \cdot 10^{-2}$	—	—
4	$3,3 \cdot 10^{-2}$	$3,0 \cdot 10^{-2}$	$2,8 \cdot 10^{-2}$	$2,7 \cdot 10^{-2}$	$1,1 \cdot 10^{-3}$	$1,2 \cdot 10^{-3}$
5	$2,4 \cdot 10^{-2}$	$2,7 \cdot 10^{-2}$	$1,2 \cdot 10^{-2}$	$1,0 \cdot 10^{-2}$	$6,0 \cdot 10^{-3}$	$6,8 \cdot 10^{-3}$
6	$4,5 \cdot 10^{-2}$	$4,0 \cdot 10^{-2}$	$3,5 \cdot 10^{-2}$	$3,5 \cdot 10^{-2}$	$1,2 \cdot 10^{-3}$	$1,3 \cdot 10^{-3}$

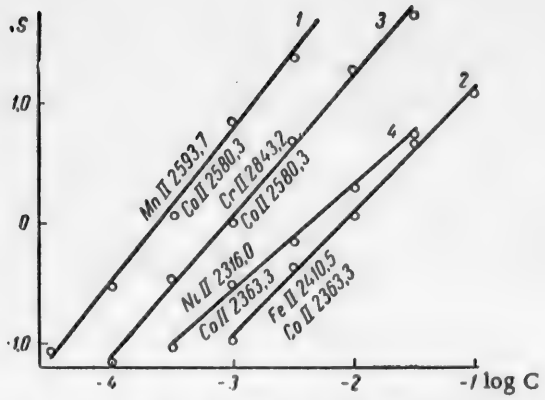

Fig. 1. Calibration curve for the determination of Mn, Cr, Ni, and Fe in Zr.

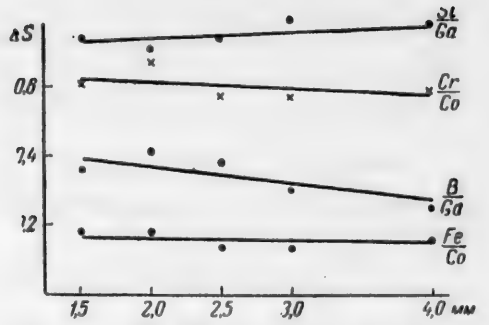

Fig. 2. Effect of interelectrode gap on blackening difference.

In order to eliminate the effect of possible changes in the evaporation conditions, and in excitation of the spectra of the impurities, and also eliminate "third" components, the internal standard method was used. The internal standards used were Co and Ga; these were introduced into both the standards and the test samples in concentrations of 1×10^{-2}% which were chosen experimentally. The analytical pairs of lines are given in Table 2, typical calibration curves are shown in Fig. 1.

The homologous character of the analytical pairs of lines was checked experimentally. As examples, on Fig. 2 are shown the curves relating difference in blackening ΔS for certain analytical pairs of lines to the interelectrode gap.

The use of internal standards made it possible to achieve a high degree of reproducibility, this amounted to, for Mn, Cr—8%, B—9%, Fe, Ni, Mg, Si, Bi, Sb, Sn, Pb—10%, Cd—11%, Al, K, Na and Li—20%*. The reliability of the method was confirmed by a comparison of the results of chemical and spectrographic determinations (Table 3).

The sensitivity of the determination of impurities in ZrO_2 is the same as that obtained for the analysis of ThO_2 and BeO [7]. It should be pointed out that this method, as a rule, is 2-3 times, and in some cases, 10 times more sensitive than the method of fractional distillation with a carrier [3], and the method of direct "combustion" of zirconium in various light sources, in which the spectra are recorded by means of spectrographs with high dispersion [1, 2].

SUMMARY

The evaporation method is applicable to the determination of a number of impurities in zirconium dioxide. Reproducible experimental results are obtained by using cobalt and gallium as internal standards.

The vacuum variant of the evaporation method is superior from the point of view of the sensitivity and reproducibility of determination of all the elements tested (with the exception of Bi, Sn, Pb, Cd, and Sb).

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DETERMINATION OF ETHOXY GROUPS IN SOME ORGANO-SILICON AND ALUMINUM COMPOUNDS

E. A. Bondarevskaya, S. V. Syavtsillo, and R. N. Potsepkina

Determination of the ethoxy group content of organosilicon compounds is based on formation of ethyl iodide [1-4]. This method is fairly sensitive and accurate. However, the necessity for a large number of reagents and special apparatus limits its application.

As for organoaluminum compounds no method has been described for determining their ethoxy group content. For this purpose, for certain organosilicon and organoaluminum compounds, we used the properties of these compounds to hydrolyze in the presence of acids or alkalis with the formation of ethanol, which can be quantitatively determined by known methods [5-8], and also by the method of oxidizing it with potassium dichromate [9].

Experimental Procedure. An aliquot of test organosilicon compound (0.12-0.15 g), fused into an ampoule, was placed in a conical flask into which 10 ml of 5% potassium dichromate and 5 ml of sulfuric acid (1 : 1) had been poured beforehand. The ampoule was broken under the level of the solution; the flask was then closed with a stopper fitted with a reflux condenser. The contents of the flask were then heated for 30 minutes on a boiling water bath; the flask was then cooled and 25 ml of 10% iodide solution added; after 5 minutes the liberated iodine was titrated with 0.1 N $Na_2S_2O_3$. A blank was carried out in parallel.

The accuracy and sensitivity of the method were established with various concentrations of ethanol (Table 1).

TABLE 1

OC_2H_5 taken, %	Sample wt., g	OC_2H_5 taken, %	Experimental error, relative %
92,44	0,0510	92,15	0,30
	0,0484	92,23	0,2
47,46	0,1448	47,64	0,4
	0,1084	47,87	0,8
28,61	0,0876	28,59	0,1
	0,0609	28,83	0,7
17,74	0,0938	17,94	1,1
	0,0470	17,96	1,2
10,46	0,2770	10,42	0,4
	0,0909	10,41	0,5
5,01	0,1124	4,99	0,4
	0,1170	5,08	1,4
1,87	0,0929	2,07	10,6
	0,0825	1,91	2,6
0,69	0,1115	0,71	3,0
	0,0992	0,68	1,4
0,10	0,1304	0,11	10,0

TABLE 2

OC_2H_5 taken, %	Sample wt., g	OC_2H_5 taken, %	Experimental error, relative %
11,44	0,1521	11,32	1,0
	0,1806	11,28	2,4
3,51	0,1758	3,44	2,0
	0,2481	3,68	5,0
8,69	0,1910	8,72	0,3
	0,2102	8,58	1,2
1,61	0,1932	1,72	7,0
	0,3532	1,49	7,0
0,53	0,2994	0,50	6,0
0,32	0,3059	0,32	0
	0,3785	0,36	12,0
0,10	0,2710	0,10	0
	0,2452	0,11	10,0

In the course of these experiments we studied whether the oxidation of ethanol obtained by the hydrolysis of diphenyldiethoxysilone, and subsequently diluted with polymer free from ethoxy groups, is quantitative (Table 2).

TABLE 3

Test material	Sample, wt.	OC_2H_5 found, %	Experimental error, relative %
Triethoxysilane	0,0721	82,66	0,4
82,31% OC_2H_5	0,0701	82,43	0,1
Tetraethoxysilane	0,1589	85,70	0,9
86,53% OC_2H_5	0,1148	85,76	0,8
Methylfluorobenzene	0,1489	39,18	0
diethoxysilane	0,1384	39,89	0,9
39,2% OC_2H_5			
Diphenyldiethoxysilane	0,1196	33,29	0,6
33,08% OC_2H_5	0,1478	33,19	0,2
Phenyltriethoxysilane	0,1384	55,84	0,8
56,25% OC_2H_5	0,1391	55,94	0,5

TABLE 4

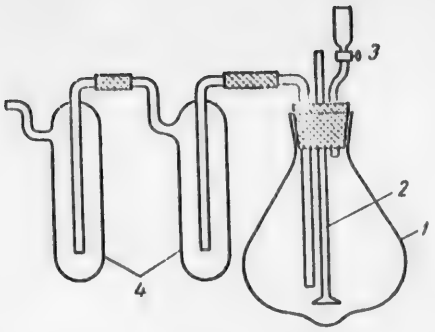
Test material	Sample wt., g	OC_2H_5, %	Experimental error, relative %
Triethoxyaluminum,	0.0731	78.98	2.0
calculated	0.1108	78.45	2.8
80.63% OC_2H_5	0.1142	79.92	0.9
	0.0996	79.50	1.0

TABLE 5

Wt. of triethylaluminum, g	OC_2H_5 obtained by	
	$K_2Cr_2O_7$, %	HI, %
0.1135	2.24	–
0.1115	2.18	–
0.0811	2.72	–
0.0395	–	2.29
0.0468	–	2.59
0.0244	–	2.76

From the results given in Tables 1 and 2 it is evident that the sensitivity of the method amounts to 0.1-0.3%; while the accuracy is up to about 12% relative. The method indicated was used for the analysis of organosilicon compounds with differing contents of ethoxy groups (Table 3).

The principle of the method described was extended to the determination of diethylethoxyaluminum as an impurity in triethylaluminum. Since triethylaluminum is oxidized violently in air, the method was modified, mainly with the aim of choosing conditions for preventing the triethylaluminum from coming into contact with air during sampling and during hydrolysis. The samples of triethylaluminum were taken in thin-walled ampoules which had been placed beforehand in a vacuum desiccator to remove the air inside them and fill them



with nitrogen free from oxygen. The bulb of an ampoule was then heated slightly and its tip rapidly immersed through an opening in the stopper of the tube containing test material. During this process nitrogen free from oxygen was bubbled vigorously through the sample. The filled ampoule was sealed off and transferred to the flask of the apparatus. Nitrogen was passed through the flask 1 (diagram) containing the sample for 12-20 minutes in order to expel the air; the ampoule was broken with the rod 2, and water added dropwise from the dropping funnel 3 until the material had decomposed completely. After this, the contents of flask 4, into which water had been poured before commencing the experiment, was quantitatively transferred into the flask; to the same flask was then added 5 ml of 5% $K_2Cr_2O_7$ and 3 ml of H_2SO_4 (1 : 1); the flask was closed with a stopper fitted with a reflux condenser, and heated on a water bath for 30 minutes; the procedure followed subsequently was the same as that indicated above. This method was used for determining the ethoxy groups in triethoxyaluminum (Table 4), and also for determining diethylethoxyaluminum as an impurity in triethylaluminum. During these determinations a comparison was made of the method described, with the method of determining ethoxy groups by means of hydrogen iodide [3] (Table 5).

From the results given in Table 5 it is clear that both methods give reproducible values.

SUMMARY

A method has been developed for determining ethoxy groups in certain organosilicon and organoaluminum compounds; it is based on the hydrolysis of the compounds examined and subsequent quantitative determination of the alcohol formed.

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QUANTITATIVE DETERMINATION OF THE COMPOSITION OF THE COPOLYMER OF TETRAFLUOROETHYLENE WITH TRIFLUOROETHYLENE BY INFRARED SPECTROSCOPY

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The method of determining the composition of the copolymer of tetrafluoroethylene ($CF_2 = CF_2$) with trifluoroethylene ($CF_2 = CFH$) is based on differences in the absorption spectra of the polymers of tetrafluoroethylene and trifluoroethylene in the region of the absorption of C-H bonds. Measurements were carried out on an IKS-11 apparatus with a LiF prism (for the region 2900-3100 cm^{-1}) and a NaCl prism (for the region 750 cm^{-1}). The absorption band of the C-H bonds in the sectors of polytrifluoroethylene and the copolymer is observed at 2987 cm^{-1}. The band at 2987 cm^{-1} and also the spectrum for polytetrafluoroethylene in this region are shown in Fig. 1. Since polytetrafluoroethylene is transparent in this region, all the absorption of the copolymer is caused by one of its components—trifluoroethylene.

The experimental procedure consists of the following. From the spectra of films of polytrifluoroethylene a curve is constructed relating the optical density at the maximum of the band at 2987 cm^{-1} (D_0) and the thickness of the films in d_1 microns (Fig. 2). The value of the optical density for 1 μ thickness of film is given by $D = 0.170$. The optical density of the copolymer at the maximum of the band 2987 cm^{-1} is then determined; from the curve (Fig. 2) the effective thickness d_1 of trifluoroethylene in the film of copolymer is determined.

The value $d_1/(d-d_1)$ (where d is the thickness of the copolymer film) gives the ratio of the effective thicknesses of trifluoroethylene and tetrafluoroethylene in the given sample of copolymer.

In order to find the ratio of the number of molecules of one component to the number of molecules of the other component (i.e., the ratio of the volume of the monomers composing the copolymer), it is necessary to multiply $d_1/(d-d_1)$ by K which is equal to $\rho_1/\rho_2 \cdot M_2/M_1$, where ρ_1, ρ_2, M_1, and M_2 are the density and molecular weight of trifluoroethylene and tetrafluoroethylene respectively. In our case K approximates to 1; accordingly, the ratio of the effective thicknesses gives the ratio of the number of molecules of the monomers which have been copolymerized, while the content of one of the components of the copolymer, e.g., trifluoroethylene (c_1) is given as a percentage by: $c_1 = d_1/d \cdot 100\%$.

The use of this technique is based on two assumptions: first, it is assumed that the volume of the copolymer is made up additively from the volumes of the polytetrafluoroethylene and polytrifluoroethylene; second, it is assumed that the absorption for one C-H group in the spectra of polytrifluoroethylene and copolymer is the same. The correctness of these assumptions is confirmed by the good results obtained during the analysis of standard samples of the copolymer by the suggested method.

The standards used for checking the method suggested were samples of copolymer whose composition had been determined by analysis of the gaseous mixture of monomers (i.e., mixtures of tetrafluoroethylene and trifluoroethylene).

The spectra of the monomers (shown in Fig. 3 [1]) were used for analyzing the gaseous mixtures. Trifluoroethylene has an absorption band at 750 cm^{-1}. Since tetrafluoroethylene does not absorb at this wave length, this band was chosen for constructing calibration curves relating optical density of the mixtures at the absorption

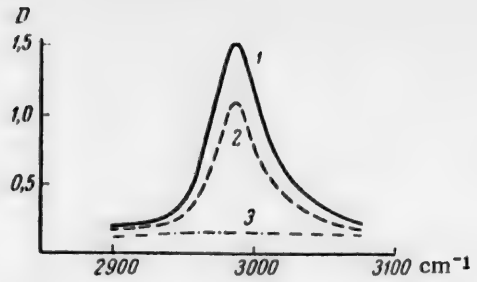

Fig. 1. 1) Polytrifluoroethylene; 2) copolymer of tetrafluoroethylene and trifluoroethylene; 3) polytrifluoroethylene.

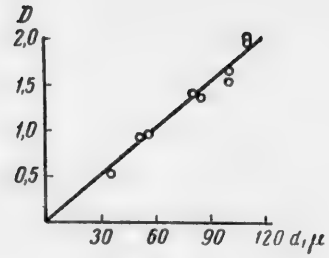

Fig. 2.

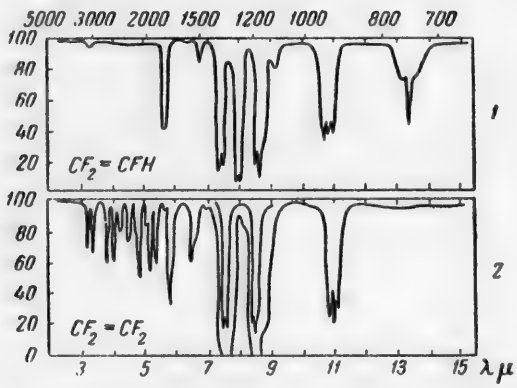

Fig. 3. 1) Trifluoroethylene; 2) tetrafluoroethylene.

Trifluoroethylene Content of Standard Samples of Copolymer, %

On the basis of the band intensity at the maximum	On the basis of analysis of gaseous mixtures of the monomers	On the basis of integral absorption
44.5	43.0	43.5
44.2	39.0	38.5
57.2	59.4	52.5
73.7	74.1	69.5
26.3	23.2	24.0

maximum to the trifluoroethylene concentration of the mixtures. The calibration curve (Fig. 4) has two linear sections with a break in the concentration range 20 to 40%. The concentration of trifluoroethylene is plotted along the abscissa while the values of the optical density of the band at 750 cm^{-1} are plotted along the ordinate. It should be pointed out that a curve with this shape is characteristic for cases where one of the components of a mixture has a C-H bond. Probably the non-linearity can be explained by the formation of association between the molecules of the gas. The spectra of the gaseous mixtures of the monomers were obtained under atmospheric pressure; the mixtures were placed in a cuvette with a layer thickness of 1 cm and with windows made of NaCl.

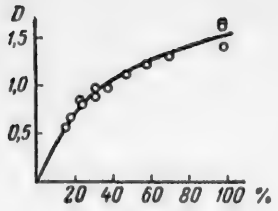

Fig. 4.

Results obtained during a comparison of the given method with the values of the standards are given in the Table. The first column of the Table contains the values of the trifluoroethylene concentrations, in percentages, for the standard samples, as determined by the method suggested. The second column contains the values of the trifluoroethylene concentrations for the same samples, but determined by analysis of the gaseous mixtures. The agreement between the two sets of results can be regarded as satisfactory. This indicates that the intensity of the absorption band for the one C-H group of trifluoroethylene is maintained in the copolymer.

A check on the determination of the composition of the copolymer on the basis of the integral intensity of the absorption band instead of on the basis of the absorption at the maximum, showed that the same direct proportionality exists between the integral intensity of the band at 2987 cm^{-1} and the film thickness. Results of this check are given in the third column of the Table.

Films of varying thicknesses were used for determining the composition of each of the copolymers tested. The scatter of results obtained during this work did not exceed 10%.

I should like to thank V. M. Chulanovskii for his interest in the work, G. I. Lapotinikova for help with the measurements, and S. G. Malkevich for samples of copolymers and mixtures of gases.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF ACRYLONITRILE BY MEANS OF PIPERIDINE

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For the quantitative determination of acrylonitrile we have used its reaction with piperidine $CH_2(CH_2-CH_2)_2NH + CH_2 = CH-CN \rightarrow CH_2(CH_2 \rightarrow CH_2)N \rightarrow CH_2CH_2CN$, which proceeds quantitatively in the presence of catalytic amounts of acetic acid. The β-(N-piperidyl)-propionitrile which is formed possesses basic properties and can be titrated with acid. An aliquot of acrylonitrile is treated with excess piperidine for 30 minutes at room temperature. Excess piperidine is bound by means of acetic anhydride, while the β-(N-piperidyl)-propionitrile is titrated with a solution of hydrochloric acid in methanol using a mixed indicator of methyl red and methylene blue. The amide and acetic acid which are formed by the interaction of piperidine and acetic anhydride do not interfere with the titration. Prior to analysis, the acrylonitrile is dried with calcium chloride and distilled. Purified dioxane is used as solvent.

Since piperidine, despite careful purification, may still contain impurities which can react with acid, and which cannot be bound with acetic anhydride, a blank is carried out. Acrylonitrile is also determined by the sulfite method for comparison [2]. Acrylic acid and its esters interfere with acrylonitrile determination. Ethylenecyanhydrin does not appear to interfere.

Sample wt., mg	Acid used for titration, ml	Acrylonitrile found, %	
		by the piperidine method	by the sulfite method
43.12	16.23	99.84	99.88
50.68	19.10	99.90	–
50.68	19.08	99.89	–
42.00	15.84	100.00	–
51.10	19.20	99.64	–
31.90	12.00	99.81	–

0.05 N hydrochloric acid in anhydrous methanol is prepared by dissolving concentrated hydrochloric acid in anhydrous methanol. The indicator used is methyl red–methylene blue (0.2 g methyl red and 0.04 g methylene blue, 60 ml methanol and 40 ml distilled water).

The determination is carried out by introducing 5 g of piperidine into a 50 ml standard flask and diluting to the mark with dioxane; the solution is then thoroughly mixed. 5 ml of this solution is pipetted into a 100 ml flask fitted with a ground glass stopper, and 30-50 mg of acrylonitrile in a sealed ampoule introduced; the

ampoule is broken with a glass rod; the rod is rinsed with dioxane and 0.2 ml of 50% acetic acid added to the mixture. The solution is shaken up and then allowed to stand for 30 minutes; 5 ml of acetic anhydride is added dropwise from a buret, followed by 3 drops of indicator solution, and the solution finally titrated with 0.05 N hydrochloric acid in methanol to the appearance of an intense raspberry color. A blank is carried out at the same time. Results for the determination of acrylonitrile are given in the Table.

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DETERMINATION OF DIBUTYLPHOSPHORIC, MONOBUTYLPHOSPHORIC, AND PHOSPHORIC ACIDS BY MEANS OF PAPER CHROMATOGRAPHY

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During a study of the radiolysis of tributylphosphate, of considerable interest was the quantitative determination of dibutylphosphoric (DBP) and monobutylphosphoric (MBP) acids; the latter are formed under the action of radiation, and show an essential effect on the processes of extraction separation of thorium, uranium, and fission products [1].

Partition chromatography on paper can be used for determining the yields of DBP and MBP. In many cases, this technique permits analysis of very small amounts of material [2-4].

Separation of mixtures on paper depends on a number of factors: adsorption on the surface, ion exchange, and partitioning between solvents. Of these, the most important factor is the latter; accordingly, the correct choice of solvent determines the success of the chromatographic separation.

Separation of DBP and MBP is most complete on using chloroform and alcohols.

In order to ensure constant values of the partition coefficients, it is usual to carry out chromatographic separation of acids in a medium containing an acid or a base [5]. We used mixtures of a base with alcohols, since DBP and MBP hydrolyze to a lesser extent in alkaline solutions [6]. In order to cut down the time of chromatographic separation, the solvent was raised to a height of 15-20 cm. For values of the height less than 15 cm, the R_f value was found to depend on the path through which the solvent passed; this is explained by the existence of a gap between the solvent front and the point on which the acid is applied.

The setup used for chromatographic separation was a glass cylinder 30 cm tall, with an internal diameter of 13 cm; it was fitted with a ground glass lid and a holder for six paper strips. A cell (Petri dish) containing the organic solvent was placed on the bottom of the cylinder. Paper made by the Volodarskii factory (GOST 5621) was used for chromatographic separation; the paper was washed with 0.1 N oxalic acid, and then with water, and, finally with alcohol.

0.02 ml of the solution of acids was placed by means of a capillary on strips of paper 2.5 cm wide, at a distance of 2 cm from the edge of the paper.

After the spots had dried out, the strip was fastened in the cylinder and the chromatograms allowed to run for 3-4 hours.

The following solvent mixtures were used for the separation:

1. Butanol–methanol–water (4 : 1 : 2).
2. Isoamyl alcohol– pyridine–25% ammonia solution (6 : 14 :20).
3. Chloroform–methanol–H_2O (4 : 5 : 1).
4. Propanol– 25% ammonia solution–water (6 : 1 : 3).
5. Methanol–25% ammonia solution–water (6 : 1 : 3).

TABLE 1

Solvent	R_f value		
	dibutylphosphoric acid	monobutylphosphoric acid	H_3PO_4
4	0.81–0.88	0.52–0.55	0.35–0.26
3	0.93–0.96	0.73–0.75	0.21–0.24
2	0.86–0.89	0.53–0.57	0.24–0.18
1	0.72–0.77	0.47–0.53	0.22–0.27
5	0.93–0.88	0.68–0.74	0.47–0.53

A mixture of 5 ml of 60% perchloric acid, 10 ml of 1 N hydrochloric acid, and 25 ml of 4% ammonium molybdate, diluted to 100 ml with water was used for establishing the position of the acid spots on the paper [4]. The chromatograms were sprayed with the mixture, dried in warm air, and heated for 7 minutes at 85°; they were then left in air in order to get saturated with moisture, and finally suspended for 5-10 minutes in a vessel containing H_2S. The developed spots were cut out, wet oxidized with a mixture of concentrated H_2SO_4 and HNO_3 (1 : 1) and the orthophosphate determined [6, 7].

Solutions of the independent components, as well as a solution of a mixture of dibutylphosphoric, monobutylphosphoric, and phosphoric acids were used for the experiments. The R_f values were calculated as the ratio of the distance through which the components had passed through to the distance through which the solvent had passed.

TABLE 2

Solvent	Dibutylphosphoric acid, γ			Monobutylphosphoric acid, γ			H_3PO_4			Total P, γ		
	taken	found	difference	taken	found	difference	taken	found	difference	taken	found	difference
1	31	33	+ 2	19	16	- 3	14	16	+ 2	64	65	+ 1
4	31	30	- 1	19	18	- 1	14	16	+ 2	64	64	0

Identification of the components on a chromatogram was carried out by comparison with the rate at which a "marker" moved. The values of the coefficients for the rate of movement of various solvents are given in Table 1.

Variations in the R_f values depend, presumably, on differences in the density of the filter papers and on temperature variations.

It should be pointed out that in the process of deciding on the ratios of the components in the system chloroform–methanol–water, under the conditions we used, we established that on using chloroform saturated with water, dibutylphosphoric acid (concentration 10^{-2}N) remains on the paper at the point where it was placed, probably as the result of its adsorption by the filter paper.

The fact that dibutylphosphoric acid is held by the paper can presumably be used for separating dibutylphosphoric acid from tributylphosphate.

Results of experiments on the quantitative determination of the components of the mixtures are given in Table 2.

The results which we obtained lead one to conclude that dibutylphosphoric, monobutylphosphoric, and phosphoric acids can be separated by partition chromatography on paper.

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V. I. KUZNETSOV

(On his fiftieth birthday)

Doctor of Chemical Sciences Vitali Ivanovich Kuznetsov, one of the leading Soviet analytical chemists, an outstanding specialist in the application of organic reagents, the author of more than 200 scientific papers, and a professor, recently celebrated his fiftieth birthday.

V. I. Kuznetsov was born on the 21st of April,1909 in the village of Uyar in Krasnoyarsk province. In 1930 he finished at Tomsk State University. He then worked in the All Union Institute of Mineral Raw Material and in other scientific institutions. At present V. I. Kuznetsov heads the laboratory of organic reagents of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR.

The main and constant theme of his research is the development and study of organic reagents for different analytical purposes: for color reactions, extraction, coprecipitation. On the basis of his work dozens of methods which have found wide practical applications have been developed in the USSR and abroad. Mention may be made of thoron, arsenazo (uranon) and their analogs anthrazo, phenazo, phenysulfazo, anthraxas, stilbazo, etc., among those reagents which he has developed.

V. I. Kuznetsov has done a great service in developing the theoretical bases of extraction separation of the elements. He was one of the first to introduce ideas regarding the various mechanisms of extraction, and to suggest a classification for the numerous extraction processes. His review article on extraction enjoys popularity among chemical specialists. V. I. Kuznetsov has also done a considerable amount of work in developing new practical techniques for the extraction separation of the elements. He has suggested a collection of low melting extractants which can be used for extracting elements over a wide acidity range.

V. I. Kuznetsov has developed a new, efficient method for coprecipitating ultra-small amounts of more than 30 elements by means of organic coprecipitants.

Under his guidance a new spectrophotometric method has been developed—thermospectrophotometry; the latter technique is of considerable importance for continuous automatic control of production.

V. I. Kuznetsov has carried out some original work in the field of organic synthesis, using complex chelate compounds. The methods he developed have made it possible to increase the reactivity of materials, and to carry out syntheses which were hitherto impossible or presented considerable experimental difficulties.

In the theory of action of organic reagents, mention should be made of the theory of the similarity between the action of organic and inorganic reagents, which has made it possible to forecast the properties of new reagents; the theory of the colors of reagents and their complexes; and also research on the properties of characteristic atomic groups and the influence of the structure of organic reagents on the stability of the complex compounds they form. V. I. Kuznetsov has suggested a new, objective method for evaluating the relative stability of complexes.

Kuznetsov has carried out a lot of work on popularizing new scientific ideas and methods in analytical chemistry so that they are adopted as rapidly as possible in industry.

The Commission on Analytical Chemistry and the Editorial Board of the Journal of Analytical Chemistry, Acad. Sci. USSR, wish V. I. Kuznetsov many years of fruitful work for the benefit of our country.

THE ANALYTICAL CHEMISTRY SECTION AT THE AT THE VIII MENDELEEV MEETING ON GENERAL AND APPLIED CHEMISTRY

(March 16-23,1959)

About 300 people from various scientific research institutes, colleges, and industrial enterprises, and also scientists from China, Bulgaria, Czechoslovakia, Poland, Hungary, and Italy took part in the work of the analytical chemistry section. About 70 reports were heard at the meetings.

In his introductory address I. P. Alimarin pointed out the successes achieved, and the modern problems of analytical chemistry.

Reports on the basic fields of analytical chemistry were widely presented: physical and physicochemical methods of analysis, the use of new organic reagents, elemental organic microanalysis, chromatographic analysis and the use of labeled atoms in analytical chemistry.

I. V. Tananaev reported on the use of the techniques of physicochemical analysis in heterogeneous systems for solving a number of the problems of analytical chemistry,

In his report on modern tendencies in the use of organic reagents, V. I. Kuznetsov, in addition to noting the successes achieved, pointed out a number of the drawbacks in the search for, and during the synthesis of,the necessary reagents. A. K. Babko, taking as examples the halogen and thiocyanate complexes, showed the connection between the stability of complexes and the position of the corresponding central atoms in D. I. Mendeleev's periodic system.

V. M. Peshkova and V. M. Bochkova reported on the stability of the oximates of Cu, Co, and Ni as a function of the structure of the oxime molecule. V. F. Toropova reported on the twofold character of the reaction of certain compounds during complex formation. The address given by Z. F. Shakhova and his coworkers A. I. Kokorina and N. A. Polotebnova touched on questions of using heteropolyacids in analytical chemistry.

A large number of reports was devoted to the application of new organic reagents in analysis. Thus, dialkyl- and diaryldithiophosphoric acids (A. I. Busev and M. I. Ivanyutin) have been used for separating a number of elements, while arylarsonic and arylphosphinic acids have been used for the same purpose (A. I. Portnov). R. P. Lastovskii and coworkers reported on some properties of new complexons. The attention of the audience was drawn by the reports of V. A. Nazarenko, G. G. Shitateva, and A. I. Kononenko on the photometric determination of a number of elements using fluorone derivatives. A. I. Cherkesov reported on the use of the "halochrome" phenomenon in analytical chemistry.

Of undoubted interest was the report of B. M. Dobkina and T. M. Malyutina on the determination of tantalum by the method of differential spectrophotometry. Deserving of attention was the communication by Yu. V. Morachevskii and I. A. Stolyarova on new, highly sensitive methods of analysis using an ultraviolet microscope.

Several reports were devoted to methodological and theoretical questions in spectrographic analysis (N. F. Zakharii and G. A. Sheinin,, E. E. Vainshtein and coworkers).

Significant successes have been achieved in improving flame photometry. (N.S.Poluéktov and M.N. Nikonov).

Several reports were devoted to the polarographic determination of the elements. (S. I. Sinyakova, Z. B. Rozhdestvenskaya and I. A. Yarova,and Ya. P. Gokhshtein). I. D. Panchenko and Yu. S. Lylikov and coworkers gave some new results on the application of solid electrodes. Kemulya (Poland) gave a very interesting report on a polarographic method for the determination of traces of metals using a suspended drop. J. Semerano (Italy) reported on the use of polarography and spectrophotometry for establishing the nature of the Me-C bond in organometallic compounds.

E. Minchevskii (Poland) discussed titration in non-aqueous media.

The communication by N. I. Udal'tsova and P. N. Palei was devoted to the use of amperometric titration with two electrodes in uranium and thorium chemistry.

Considerable attention was devoted to chromatographic research.

M. M. Senyavin demonstrated the possibility of forecasting the conditions for chromatographic separation of elements on the basis of the position of the elements in the Mendeleev periodic system. T. A. Belyavskaya reported on the use of ion exchange for studying the state of materials in solution.

Interesting reports were heard on the chromatographic separation of a number of elements (A. S. Vernidub and V. I. Petrashen'), on the problem of regulating the properties of ion exchange resins(N.G.Polyanskii), on the chromatographic detection of sulfanilamide preparations in the liquids of organisms (F. M. Shemyakin and coworkers), and also on the use of high polymers in chromatographic analysis (G. L. Starobinets and coworkers). Two reports were devoted to gas chromatography (A. A. Zhukhovitskii and N. M. Turkel'taub, and G. Shai-Hungary).

Several reports were devoted to the use of radioactive isotopes for studying the processes of complex formation by a chromatographic method (D. I. Ryabchikov and coworkers). for studying the mechanism of the coprecipitation of the ions of rare metals with sulfides (N. A. Rudnev), and for the determination of rare elements by the method of isotopic dilution (I. P. Alimarin and G. N. Bilimovich).

Of the communications on elemental organic microanalysis, one should point out the reports of M. O. Korshun, N. E. Gel'man, and V. A. Klimova and coworkers on the development of rapid micromethods with simultaneous determination of several elements on one aliquot of boron-, fluoro- and silico-organic compounds.

Of the reports of foreign scientists, of particular interest was the communication by Professor Liu Ta-kang (China) on the present state of research on rare elements in China. The professor brought a gift of a collection of rare earths for the Soviet Union.

The proceedings at the various sessions were lively; valuable suggestions and recommendations were put forward.

G. N. Bilimovich

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